PB82-119447

The Potential Atmospheric Impact of Chemicals Released to the Environment Proceedings of Four Workshops

(U.S.) National Oceanic and Atmospheric
Administration, Silver Spring, MD

Prepared for

Environmental Protection Agency
Washington, DC

Jan 81

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington DC 20460

EPA 560/5-80-001
January 1981

PB82-119447

Toxic Substances

EPA

The Potential Atmospheric Impact of Chemicals Released to the Environment

Proceedings of Four Workshops

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. EPA 560/5-80-001	2.	3. Recipient's Accession No. PB82 119587

4. Title and Subtitle
THE POTENTIAL ATMOSPHERIC IMPACT OF CHEMICALS RELEASED TO THE ENVIRONMENT.
Proceedings of Four Workshops

5. Report Date
12/80 (Date of Issue)

6.

7. Author(s)
JOHN M. MILLER (editor) NAT'L OCEANIC & ATMOSPHERIC ADMIN.

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
AIR RESOURCES LABORATORIES
NAT'L OCEANIC & ATMOSPHERIC ADMINISTRATION
SILVER SPRING, MD 20910

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C)
(G) IAG 98120AOTE

12. Sponsoring Organization Name and Address
ENVIRONMENTAL PROTECTION AGENCY
401 M STREET, SW
WASHINGTON, DC 20460

13. Type of Report & Period Covered
WORKSHOP REPORT

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

Four workshops are reported: toxic substances in atmospheric deposition, screening chemicals for inadvertent modification of the stratosphere, the impact of chemicals on the radiative transfer imbalance, and the impact of anthropogenic chemicals on precipitation processes. These workshops were convened as part of an effort to assess the impact of toxic chemicals on the abiotic environment (specifically, the atmosphere), to assess the feasibility of screening chemicals for these impacts, and whenever possible to develop a screening logic. Report contains an extensive literature survey and bibliography.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms

Toxic Substances, screening for effects, atmospheric deposition, stratospheric ozone depletion, radiative transfer imbalance, precipitation modification, atmospheric modification.

c. COSATI Field/Group

18. Availability Statement Release Unlimited	19. Security Class (This Report) Unclassified	21. No. of Pages 240
	20. Security Class (This Page)	22. Price

(See ANSI–Z39.18) *See Instructions on Reverse*

OPTIONAL FORM 272 (4–77)
(Formerly NTIS–35)
Department of Commerce

EPA 560/5-80-001
January 1981

THE POTENTIAL ATMOSPHERIC IMPACT OF CHEMICALS RELEASED TO THE ENVIRONMENT
Proceedings of Four Workshops

Edited by
John M. Miller
Air Resources Laboratories
National Oceanic and Atmospheric Administration
Silver Spring, MD 20910

98120AOTE

Project Officer
William Wood
Office of Toxic Substances
U.S. Environmental Protection Agency
Washington, DC 20460

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
WASHINGTON, DC 20460

This document has been reviewed and approved for publication by the Office of Toxic Substances, U.S. Environmental Protection Agency. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

The report of a workshop on
TOXIC SUBSTANCES IN ATMOSPHERIC DEPOSITION
has been distributed also as a report of
the National Atmospheric Deposition Program

FOREWORD

In the Toxic Substances Control Act of 1976, the Congress expressed the finding that human beings and the environment are being exposed each year to a large number of chemical substances and mixtures, and that the effects of many on health and environment are uncertain. Congress decided therefore that (1) adequate data should be developed with respect to the effect of chemical substances and mixtures on health and the environment and that such data should be the responsibility of those who manufacture and those who process such chemical substances and mixtures; (2) adequate authority should exist to regulate chemical substances and mixtures which present an unreasonable risk of injury to health or the environment; and (3) authority over substances and mixtures should be exercised in such a manner as not to impede duly or create unnecessary economic barriers to technological innovation.

EPA is developing scientific risk assessment methodologies which balance the primary purpose of TSCA, to assure that chemical substances do not present an unreasonable risk, with the admonition that the Agency not unduly impede innovation in the chemical industry. Development of these methodologies has involved the identification of which health and environmental effects EPA should consider to be important, the identification of the information needed for a risk assessment, the organization of this information into a logical assessment scheme, the development of decision criteria to trigger testing, and the identification and development of testing methods.

As part of this activity EPA is soliciting the guidance of the scientific community. The workshops addressed in this volume are a series sponsored by the Agency on the topic of screening chemicals for atmospheric modification and its effects.

James J. Reisa

James J. Reisa, Ph.D.
Associate Deputy Assistant Administrator
for Toxic Substances
U.S. Environmental Protection Agency

THE POTENTIAL ATMOSPHERIC IMPACT OF CHEMICALS RELEASED TO THE ENVIRONMENT

CONTENTS

Page

FOREWORD iii

ABSTRACT vi

Report of a workshop on TOXIC SUBSTANCES IN ATMOSPHERIC DEPOSITION
  Table of Contents 3

Report of a workshop on SCREENING CHEMICALS FOR INADVERTENT MODIFICATION OF THE STRATOSPHERE
  Table of Contents 149

Report of a workshop on THE IMPACT OF CHEMICALS ON THE RADIATIVE TRANSFER IMBALANCE
  Table of Contents 169

Report of a workshop on ANTHROPOGENIC CHEMICALS AS MODIFIERS OF CLOUDS AND PRECIPITATION
  Table of Contents 193

Preceding page blank

ABSTRACT

Four workshops are reported: toxic substances in atmospheric deposition, screening chemicals for inadvertent modification of the stratosphere, the impact of chemicals on the radiative transfer imbalance, and the impact of anthropogenic chemicals on precipitation processes.

Report of a Workshop on

TOXIC SUBSTANCES IN ATMOSPHERIC DEPOSITION:

A REVIEW AND ASSESSMENT

Jekyll Island, Georgia

November 1979

Edited by

James N. Galloway
Steven J. Eisenreich
Bryan C. Scott

PARTICIPANTS AND CONTRIBUTORS

Deborah A. Banning
Department of Environmental
Sciences
University of Virginia
Charlottesville, Virginia

L. A. Barrie
Atmospheric Environment Service
Downview, Ontario, Canada

T. F. Bidleman
Department of Chemistry
University of South Carolina
Columbia, South Carolina

Anthony R. Davis
Water Quality Branch
Inland Waters Directorate
Ottawa, Ontario, Canada

Steven J. Eisenreich
Environmental Engineering
University of Minnesota
Minneapolis, Minnesota

James N. Galloway
Department of Environmental
Sciences
University of Virginia
Charlottesville, Virginia

Donald F. Gatz
Illinois State Water Survey
Urbana, Illinois

C. S. Giam
Department of Oceanography
Texas A & M
College Station, Texas

Ronald A. N. McLean
DOMTAR Research Center
Senneville, Quebec, Canada

William Wood
Environmental Protection Agency
Washington, D.C.

John M. Miller
Air Resources Laboratories
NOAA/ERL
Silver Spring, Maryland

Michael D. Mullin
Large Lakes Research Station
Grosse Ile, Michigan

Thomas J. Murphy
Chemistry Department
DePaul University
Chicago, Illinois

Stephen A. Norton
Department of Geological Sciences
University of Maine
Orono, Maine

Donald H. Pack
Certified Consulting
Meteorologist
McLean, Virginia

Francis J. Priznar
Normandeau Associates
25 Nashua Road
Bedford, New Hampshire

Bryan C. Scott
Battelle Pacific Northwest
Laboratories
Richland, Washington

David Thornton
Environmental Engineering
University of Minnesota
Minneapolis, Minnesota

Herbert L. Volchok
Environmental Measurements
Laboratory
U.S. Department of Energy
New York, New York

TOXIC SUBSTANCES IN ATMOSPHERIC DEPOSITION

CONTENTS

Page

PARTICIPANTS AND CONTRIBUTORS 2

PREFACE 9

ACKNOWLEDGMENTS 10

INTRODUCTION 11

EXECUTIVE SUMMARY 13

PART I: TRACE METALS: A REVIEW AND ASSESSMENT 19

- 1. Introduction 19
- 2. Concentrations: Naturally and Anthropogenically Controlled 20
  - 2.1. Comparison of Emission Rates 20
  - 2.2. Comparison of Atmospheric Concentrations 22
  - 2.3. Determination of Historical Trends in Deposition 24
  - 2.4. Comparison of the Three Techniques 27
- 3. Concentration of Metals in the Atmosphere 27
- 4. Concentration of Metals in Wet Deposition 29
- 5. Deposition of Metals from the Atmosphere 39
  - 5.1. Deposition in Remote, Rural, and Urban Environments 39
  - 5.2. The Relative Importance of Dry versus Wet Deposition 39
  - 5.3. Physical Characteristics of Metals and Their Compounds Affecting Atmospheric Deposition 44
    - 5.3.1. Vapor Pressure 44
    - 5.3.2. Particle Size 46
    - 5.3.3. Solubility 48
  - 5.4. Measurement of Wet Deposition 48
  - 5.5. Measurement of Dry Deposition 50

Page

6. Potential Effects of Increases of Concentration of Metals in Atmospheric Deposition 51

  6.1. Recommended Upper Limits in Water 51
  6.2. Metal Speciation in Relation to Toxicity 51

7. Summary 54

8. Research Recommendations 55

9. References 55

APPENDIX A: Concentrations of Metals in the Atmosphere: Selected Data 64

APPENDIX B: Concentrations of Metals in Wet Deposition 72

PART II: TRACE ORGANICS: A REVIEW AND ASSESSMENT 83

1. Introduction 83

2. Vapor and Particle Distribution of Atmospheric Organics 85

3. Transfer of Gases Across Air/Water Interface 91

  3.1. Resistance to Air/Water Interface 92
  3.2. Problems 95

4. Wet Removal of Trace Organics from the Atmosphere 95

5. Dry Deposition of Particulates 97

6. Sources of Trace Organics to the Atmosphere 98

  6.1. Sources I 98
  6.2. Sources II 100

7. Variability of Concentrations and Fluxes 100

8. Atmospheric Concentrations 100

9. Total Deposition in Urban, Rural, and Remote Environments 103

10. Applications of Flux Calculations: Atmospheric PCB Input to the Great Lakes 105

  10.1. Dry Deposition 105
  10.2. Wet Deposition 106

Page

11. Research Recommendations 109

12. References 110

PART III: GUIDE FOR ESTIMATING DEPOSITION RATES OF GASES AND AEROSOLS 114

1. Introduction 114

2. Wet Removal and Deposition of Aerosols and Gases 115

    2.1. Wet Removal of Aerosols 115

        2.1.1. Attachment 115
        2.1.2. Removal 118

    2.2. Wet Deposition of Aerosols 120

        2.2.1. Air Concentrations 120
        2.2.2. Wet-Deposition Rates 120

    2.3. Wet Removal of Gases 121
    2.4. Wet Deposition of Gases 123

3. Dry Removal and Deposition of Aerosols and Gases 123

    3.1. Dry Removal of Aerosols 124
    3.2. Dry Deposition of Aerosols 125
    3.3. Dry Deposition of Gases 125

4. Relative Removal by Wet and Dry Processes 127

5. Special Situations 128

    5.1. Unique Emission Configurations 128
    5.2. Unique Receptor Configurations 129
    5.3. Unique Meteorological Environments 130

        5.3.1. Coastal Areas 130
        5.3.2. Precipitation Extremes 130

6. Research Recommendations 131

7. References 131

BIBLIOGRAPHY 134

FIGURES

Part I. Trace Metals

Figure Page

1. EF_{crust} values for atmospheric trace metals collected in the North Atlantic westerlies from R/V Trident, Bermuda, and at the South Pole 23
2. Element concentrations versus depth in sediment of Woodhull Lake, New York 25
3. Pb concentration as a function of depth in the sediments of three lakes 26
4. Airflow over the United States 33
5. Average deposition of Pb by precipitation 34
6. Average deposition of Zn by precipitation 34
7. Median concentrations of metals in precipitation in remote, rural, and urban areas relative to organism-toxicity levels 52

Part II. Trace Organics

1. Atmospheric input of anthropogenic organics to natural waters 84
2. Vapor-aerosol distributions calculated from vapor pressure and the quantity of atmospheric particulates 86

Part III. Guide for Estimating Deposition Rates

1. Collision efficiency as a function of size of the collected particles 116
2. Theoretical growth curves for solution droplets of sulfuric acid and some inorganic salts of interest at 25°C 116
3. Growth of aerosol composed of 50% ammonium sulfate 117
4. Variation of washout ratio, W, with the mass median diameter at the distance from the urban sources for St. Louis and Chilton, United Kingdom 119

TABLES

Part I. Trace Metals

Table Page

1. Global mobilization factors based on annual emission rates 21

2. Three techniques for determining the influence of anthropogenic processes on the concentration of metals in atmospheric deposition 28

3. Ranges of metal concentrations in the atmosphere 30

4. Approximate median concentrations of metals in the atmosphere 31

5. Ratios of median concentrations of metals in the atmosphere 32

6. Ranges of metal concentrations in wet deposition (rain, snow, and ice) 36

7. Median concentrations of metals in wet deposition (rain, snow, and ice) 37

8. Ratios of median concentrations of metals in wet deposition (rain, snow, and ice) 38

9. Selected values of atmospheric-deposition rates for metals in remote, rural, and urban areas 40

10. Means of data reported from all seasons for dry fraction of total deposition 44

11. Vapor pressures and boiling points of metals and their common oxides 45

12. Mass median diameter of toxic metals in aerosols 47

13. Solubility of common oxides, sulfates, chlorides, and nitrates of metals at 20° C 49

14. Recommended upper limits for metal concentrations in water 53

Part II. Trace Organics

1. Vapor pressures of trace-organic compounds 87

Table Page

2. Apparent particulate- and gas-phase distributions for organics in urban air 88

3. Ranges of gas-particulate distribution factors for organics, nitrates, and sulfates in Pasadena CA 89

4. Particulate- and vapor-phase distributions for atmospheric PCBs 90

5. Particle-size distributions for PAHs in ambient aerosols in urban, rural, and coastal areas 91

6. Water solubilities of trace-organic compounds 93

7. Henry's law constants 94

8. Washout ratios for trace-organic compounds 96

9. Dry-deposition velocities 99

10. Atmospheric concentrations of trace-organic compounds in urban and rural environments 101

11. Atmospheric concentrations of PAHs in different environments 102

12. Atmospheric concentrations and fluxes of PCBs in different environments 103

13. Atmospheric fluxes of trace-organic compounds to rural environments 104

14. Parameters for PCB flux to the Great Lakes 107

15. Atmospheric flux of PCBs to the Great Lakes 108

Part III. Guide for Estimating Deposition Rates

1. Washout Ratios 121

2. Particle-deposition velocities 125

3. Ranges of V_d for a substance with a Jekyll number <10 127

PREFACE

Our knowledge of the effect of human activities on atmospheric deposition is essentially limited to three elements (S, N, H) in the periodic table. It is generally known that there are other elements in atmospheric deposition and that their concentrations have been enhanced in recent years, but little specific and systematic detail exists on their temporal and spatial trends. To establish the state of the art, a workshop was convened in November 1979 to assess what is known and unknown about toxic metal and organic compounds in atmospheric deposition.

This assessment was made at the request of the Environmental Protection Agency (EPA), the National Oceanic and Atmospheric Administration (NOAA), and the National Atmospheric Deposition Program (NADP) to determine the pathways of removal of toxic substances from the atmosphere; the actual concentrations of metal and organic compounds in atmospheric deposition; the degree that human activities contribute to observed concentrations in atmospheric deposition in urban, rural and remote areas; and the possible threat to the environment.

The workshop, held on Jekyll Island, Georgia, was composed of three working groups. The depositional processes group was concerned with describing the specific processes and critical parameters that remove toxic substances from the atmosphere. The groups on toxic metals and on organic compounds in atmospheric deposition addressed two questions:

(1) What is known or can be predicted about the depositional processes of metal and organic compounds?
(2) What are the relative contributions of natural and anthropogenic processes to the concentration of metal and organic compounds in atmospheric deposition?

ACKNOWLEDGMENTS

As organizers, we thank EPA, NOAA, and the National Atmospheric Deposition Program for giving us the opportunity to have this workshop. Very special thanks go to Tamara Gardner for providing all the logistical support for the workshop (under, at times, arduous conditions) and for masterminding the preparation of this report and to Mary-Scott Marston for being creative and accurate in her editing. Finally we deeply appreciate the long hours of preparation, participation, and writing of the attendees.

JNG
SJE
BCS

INTRODUCTION

The number of observations on atmospheric deposition and its composition has substantially increased since the first observations of Noah[1], Little[2], Barrinchins[3], and Smith[4]. In the middle 1960s, several investigations began on the temporal and spatial trends in the composition of atmospheric deposition. As a result of this work precipitation networks were established and research on the effects of atmospheric deposition was accelerated. Most past studies focused primarily on three elements in the periodic table, S, N, and H, with a secondary focus on Na, K, Ca, Mg, and Cl. There has been a paucity of research on metal and organic compounds in atmospheric deposition.

Similarly, little systematic attention has been paid to concentrations in precipitation and atmospheric deposition rates of metal and organic compounds in different regions of the world. Therefore the assessment of our current state of knowledge was easy (especially for organic compounds)--we know very little. This ignorance is not healthy, literally or figuratively. Our deliberations have shown that for both metal and organic compounds current concentrations in atmospheric deposition exceed the limits established to reduce the effects on humans and other organisms. It is crucial that the present data base be systematically expanded so that the same questions are not still being discussed ten years from now.

The reports of the working groups on metal compounds and on organic compounds in atmospheric deposition are in part literature reviews of existing information and assessments of the present state of our knowledge of the impact of human activities on metal and organic compounds in atmospheric deposition. Specific questions are addressed:

(1) What are the toxic metal and organic compounds?
(2) What is the relative importance of natural versus anthropogenic processes acting as atmospheric sources for these substances?
(3) What are their concentrations in wet deposition in remote, rural, and urban areas?
(4) What are their depositional fluxes in remote, rural, and urban areas?
(5) What is the relative importance of dry versus wet deposition?

---

[1] Genesis 7:12; [2] Little, C., in The Sky is Falling! The Sky is Falling! (date unknown) public domain; [3] Cited in Hjarne, Acta et Tentamina Chemica Holmiensia 2, 23 (1753) (Stockholm); [4] Smith, R. A., Air and Rain: The Beginnings of a Chemical Climatology. London: Longmans, Green and Co. (1872) 617 pp.

(6) What are the water-quality criteria for man and other organisms relative to the concentrations in precipitation?

The report of the working group on depositional processes describes the properties of the gases and aerosols that control the relative importance of wet and dry deposition. Simple rules for estimating wet- and dry-depositional rates are presented in terms of washout ratios and depositional velocities.

Each report contains recommendations for research. These recommendations concentrate on those areas where the extent of our ignorance is especially profound. It was the consensus that additional data are needed on more metal and organic compounds before the impact of toxic metals and organic compounds in atmospheric deposition can be assessed.

EXECUTIVE SUMMARY

Part I. TRACE METALS

Information on nineteen metals in atmospheric deposition potentially toxic to humans and other organisms was assimilated to determine if metal concentrations are increasing in atmospheric deposition and if these concentrations threaten human or organism health.

On the basis of rates of emission, atmospheric concentrations, and known temporal trends in deposition, the greatest increases in concentrations of metals in atmospheric deposition due to human activity are expected for Ag, Cd, Cu, Pb, Sb, Se, Zn, with smaller increases expected for Cr and V and with little or no increases expected for Co, Mn, and Ni. There were insufficient data to rank Mo, As, Be, Sn, Te, and Tl.

Although actual data on these metals in atmospheric deposition are limited, the data available supported these expectations. The metals Zn, Pb, Cu, Mn, Ag, As, and V had measured concentrations 30 to 200 times higher in atmospheric concentration or deposition in rural, continental areas than at remote areas such as the South Pole. Other metals, Sb, Se, Cr, and Ni, had concentrations that were 10 to 30 times greater in rural areas than in remote areas.

Metals can be deposited either wet or dry from the atmosphere. An assessment of the relative importance of the two processes revealed that, depending on the metal and the area, dry deposition can be as great as or greater than wet deposition.

From analyses of vapor pressures of metals and metal oxides, only Hg, As, Se, and possibly Cd could be expected to have a significant fraction of their atmospheric concentration in the vapor phase.

In regard to the effects of increased metal concentrations in atmospheric deposition, only Pb and Hg are currently in precipitation in some areas at levels greater than the drinking-water standard. Cd, Cu, Hg, Pb, and Zn can be present in precipitation at levels higher than the standards for effects on other organisms.

Research Recommendations

Assimilating the work on metals in atmospheric deposition was less difficult than it might have been because so little has been done in spite of the scope of the problem. To avoid this in the future, we propose the following research recommendations.

(1) More data must be acquired through more studies, including the analysis of more metals.
(2) The concentration of soluble versus insoluble metals in rain and melted snow should be determined under the assumption that soluble metals are probably more mobile in the environment.
(3) Sampling and analytical methods must be standardized throughout the scientific community for all metals, including those that take on different forms in the atmosphere (i.e., Hg, As).
(4) Since dry deposition can be just as important as, if not more important than, wet deposition, standardized collection procedures must be developed.
(5) A detailed study of the metal compounds that predominate in rain and snow must be conducted.
(6) The size distribution of metals in urban, rural, and remote atmospheres needs to be determined.
(7) The fate of metals deposited in aquatic and terrestrial ecosystems must be determined.
(8) A national network to determine the temporal and spatial trends of metals in atmospheric deposition must be established.

Part II. TRACE ORGANICS

Atmospheric transport and deposition may be significant contributors to the distribution and accumulation of trace organics in the biotic and abiotic compartments of the aquatic ecosystem. Trace organics, such as polychlorinated biphenyls (PCBs), chlorinated hydrocarbon pesticides (CH), and polycyclic aromatic hydrocarbons (PAHs), are emitted into the atmosphere from sanitary landfills and municipal incinerators (PCBs, CH), aerial application to forests or crops (CH), and the high-temperature combustion of fossil fuels (PAHs). Airborne trace organics are distributed between the gas and particle phases; the relative importance of each depends on compound vapor pressure, type and quantity of absorptive surface area, and emission-source strength. Once in the atmosphere, airborne contaminants are removed by either wet or dry removal processes. PCBs and DDT remain in the atmosphere for approximately 5 to 10 days. Gas-phase organics can be removed by precipitation scavenging and direct partitioning across the air/water interface, both processes depending on the magnitude of Henry's law constant. Particle-phase trace organics are usually associated with submicron-size particles and are removed by precipitation scavenging ($W \sim 10^5$) and impaction on a water surface ($V_d \sim 0.1\text{-}1.0$ cm s^{-1}).

Numerous reports and the literature published over the past ten years were reviewed to assemble values for concentrations of trace organics in the atmosphere and in precipitation. At present, a paucity of data on trace organics in the atmosphere is readily evident. Ranges and, where possible, medians of trace-organic concentrations in the vapor and particle and in the rain and snow phases in both urban and rural areas were compiled. With simplified parameterizations of wet- and dry-deposition processes, fluxes of trace organics to water surfaces were calculated. These should be interpreted as order-of-magnitude estimates only. Conservative estimates of trace-organic fluxes suggest that dry deposition dominates wet deposition for all compounds studied.

The application of flux calculations to atmospheric PCB input to the Great Lakes has been included. Atmospheric input to aquatic systems is the major source of trace organics for lakes lacking surface sources and having large surface-area/basin-area ratios. The Great Lakes and remote inland lakes, therefore, receive 50% to 100% of their trace-organic burden from the atmosphere.

Research Recommendations

Implementing the following research recommendations is necessary to relieve the paucity of data on trace organics in the atmosphere and their deposition and effects.

(1) Methods must be developed to distinguish between vapor- and particulate-phase, high-molecular-weight organics in the atmosphere.
(2) The relationship between the mass median diameter, the deposition velocity, and the receptor surface for atmospheric particles must be established.
(3) The size distribution of atmospheric particulates containing high-molecular-weight organics must be determined.
(4) Collection methods for dry deposition of particulate- and vapor-phase organics should be developed since this is an important fraction of total deposition.
(5) The collection efficiency of different receptor surfaces for particulate- and vapor-phase organics must be determined.
(6) Accurate data on vapor pressures and water solubilities of slightly soluble, high-molecular-weight organics need to be developed.
(7) The fugacities (true dissolved fraction) of trace organics in water need to be developed.

(8) The trace-organic compositions of rain and snow and of the aerosol and gas phases in the atmosphere need to be determined before accurate deposition rates and ecological or health impacts can be evaluated.

Part III. GUIDE FOR ESTIMATING DEPOSITION RATES OF GASES AND AEROSOLS

This section provides procedures for predicting deposition of gases and aerosols that are uniformly distributed in the lowest several kilometers of the atmosphere.

Wet Deposition of Gases and Aerosols

To compute the wet deposition of a material, it is necessary to have information about the atmospheric state of the material (gas or aerosol), the anticipated air concentration, and the likely precipitation rates and durations. The wet depositions of aerosols and of gases are expressed in terms of the washout ratio. For the wet removal of aerosols, the washout ratio is parameterized in terms of the particle size and the type of rainfall (convective vs. continuous). For the wet removal of gases, the washout ratio is approximated from the inverse of Henry's law constant.

Dry Deposition of Gases and Aerosols

The dry depositions of gases and of aerosols are expressed in terms of deposition velocity. Aerosol-deposition velocities are parameterized in terms of an anticipated mean particle size and in terms of surface characteristics (land vs. water). The dry deposition of gases is so complex and variable that no attempt was made to generalize the deposition velocity; rather, a first approach to making an order-of-magnitude estimate of gas deposition velocity is outlined.

Our primary conclusion was that the predicted deposition rates should be within a factor of two or three of the true values if the computations are carried out over time and space scales on the order of 1 yr and 100 km. Improved accuracy requires a more sophisticated approach than could be provided here; however, references to such approaches have been given.

Research Recommendations

The research recommendations below are mandatory if the uncertainty inherent in deposition calculations is to be alleviated:

(1) Washout ratios for aerosols must be classified by storm type, location, season, rainfall rate, size, and mass median diameter over many locations and seasons.

(2) Gases must be grouped by their chemical and physical properties to determine if such categorization relates to the deposition properties.

(3) How much gas is reemitted to the atmosphere after initial deposition must be determined. Many gases are transported to the surface but may be reemitted to the atmosphere after the precipitation is deposited on the ground.

(4) Extensive measurements of the deposition velocity to various surfaces (snow and ice fields, water surfaces, grasslands and, especially, forests) are necessary to define dry deposition of aerosols more precisely.

(5) The importance of dry deposition of a given (previously unknown) gas to total deposition should be established through further development, and eventual standardization and refinement, of the use of the Jekyll number.

TOXIC SUBSTANCES IN ATMOSPHERIC DEPOSITION: A REVIEW AND ASSESSMENT

Part I

TRACE METALS: A REVIEW AND ASSESSMENT

J. N. Galloway (Co-chairman), H. L. Volchok (Co-chairman),
D. Thornton, S. A. Norton and R. A. N. McLean

1. INTRODUCTION

The passage of metals through the atmosphere is integral to biogeochemical cycling. Because of the dynamic nature of the atmosphere, metals can be deposited in areas remote from the initial source. Historically, the rate of deposition has been low because of the low volatility of most metals. However, with the advent of high-temperature anthropogenic processes (smelting and fossil-fuel combustion), the rate of emission for some metals has substantially increased. With increased emissions have come increases in metal concentrations in the atmosphere and in atmospheric deposition. Because of the known toxicity of some of these metals to humans and other organisms, this workshop was convened in part to assess the present knowledge of toxic metals in atmospheric deposition.

Metals classified as toxic or potentially toxic to humans and other organisms (Ag, As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Te, Tl, V, and Zn; Wood 1974) have all been found in atmospheric deposition. Several critical questions need to be asked to assess the potential risk of these metals to human health and the welfare of organisms and ecosystems:

(1) What is the relative importance of natural versus anthropogenic processes acting as sources of metals in the atmosphere?
(2) What are the metal concentrations in the atmosphere in remote, rural, and urban areas?
(3) What are the metal concentrations in precipitation in remote, rural, and urban areas?
(4) What are the depositional fluxes of metals in remote, rural, and urban areas?
(5) What is the relative importance of dry versus wet deposition?
(6) What are the water-quality criteria for humans and other organisms?
(7) What is the relationship between speciation and toxicity of the metals in atmospheric deposition?
(8) Where should future research be directed to fill in the gaps in our knowledge?

Preceding page blank

2. CONCENTRATIONS: NATURALLY OR ANTHROPOGENICALLY CONTROLLED

There are three ways to assess whether anthropogenic or natural emission processes control current concentrations of metals in precipitation:

(1) Compare the actual metal-emission rates of natural and anthropogenic processes;
(2) Compare the ratios of atmospheric concentrations of metals to the ratios of concentrations in source materials;
(3) Determine temporal trends in the composition of metals in atmospheric deposition.

These three techniques--emission to, concentration in, and deposition from the atmosphere--are used to analyze the different parts of the atmospheric cycle of metals to determine the impact of anthropogenic processes on metal concentrations in atmospheric deposition.

2.1 Comparison of Emission Rates

On a global basis, the known natural sources of metals in the atmosphere are injection of soil and volcanic dust and gaseous emanations. The anthropogenic emissions are from industrial gases and particulates and combustion of fossil fuels. To estimate the magnitude of the natural and anthropogenic fluxes on a global basis, a recent analysis (Lantzy and Mackenzie 1979) has been used to calculate a Mobilization Factor (MF) (Table I-1) where

$$\text{MF} = \frac{\text{Emission rate from anthropogenic sources}}{\text{Emission rate from natural sources}}$$

An analysis of the calculated MF shows that the metals that would be expected to be enriched in the atmosphere (and subsequently in atmospheric deposition) by anthropogenic processes are Pb > Ag > Sb, Mo > Zn, Cd > Cu > Sn > V, As, Se, Ni > Cr > Mn, Co, Hg.

Using quite different methods, another study estimated the global intensity of natural and anthropogenic emissions (Nriagu 1979) for some toxic metals. Although the emission rates obtained were different from those in Table I-1 (in 10^8 g y^{-1}: natural--Cd-8.3, Cu-185, Ni-260, Pb-245, and Zn-435; anthropogenic--Cd-73, Cu-560, Ni-470, Pb-4500, Zn-3140), the order of mobilization factors was the same: Pb > Cd > Zn > Cu > Ni. The absolute degree of enrichment of the metal is dependent on (1) the spatial scale used, (2) the amount of metal that is deposited close to the source, and (3) the accuracy of our estimate of the natural and anthropogenic emission rates.

Table I-1. Global Mobilization Factors Based on Annual Emission Rates

	Emissions (10^8 g y^{-1})		
	Natural	Anthropogenic	Mobilization factor
Ag	0.6	50	83
As	28 [210]	780	3.3
Cd	2.9	55	19
Co	70	50	0.71
Cr	580	940	1.6
Cu	190	2,600	13
Hg	0.4 [250]	110	0.44
Mn	6,100	3,200	0.53
Mo	11	510	45
Ni	280	980	3.5
Pb	59	20,000	340
Sb	9.8	380	39
Se	4.1 [30]	140	4.7
Sn	52	430	8.3
V	650	2,100	3.2
Zn	360	8,400	23

Source: Adapted from Lantzy and Mackenzie 1979.

NOTE: Natural emissions = Soil dust + volcanic dust and volcanic-emanation fluxes. For elements with known volatile species in the atmosphere (As, Hg, and Se), vapor emissions (in brackets) from land and sea were added to dust emissions (Lantzy and Mackenzie 1979). Anthropogenic emissions = fossil-fuel and industrial-particulate fluxes.

Relative to the first point, the MF values in Table I-1 are calculated for the global scale; if this scale were reduced to the area of the United States, the MF values would certainly increase because of a greater density of anthropogenic processes relative to the global average. On the second point, the calculated MF values show that the atmospheric emissions of many metals from anthropogenic processes are certainly greater than those from natural processes. However, this analysis assumes that for all metals except As, Hg, and Se only soils and volcanoes are the important natural sources. However, as Lantzy and Mackenzie (1979) pointed out, there is a possible net flux of metals into the atmosphere from vegetation, oceans, and low-temperature volatilization from soils of vapor-phase metals or metal compounds.

Therefore, on the scale of the United States, the MF values will be larger than those in Table I-1, but if there are additional natural sources these increases may be reduced. Since the primary focus of this report is to determine if metals are in higher concentration in atmospheric deposition because of anthropogenic activities, we will accept the limitations of the MF values and compare the ranking of metals expected to be in increased concentrations in atmospheric deposition with the results from the other techniques.

2.2 Comparison of Atmospheric Concentrations

The second technique compares elemental ratios of atmospheric concentrations with concentration ratios in the earth's crust. The function commonly used is the Enrichment Factor, EF:

$$EF = \frac{[Me]/[Al]_{air}}{[Me]/[Al]_{crust}}$$

where, if EF > 1, a metal, Me, is enriched in the atmosphere relative to its concentration in the crust, which implies a source other than the crust; where, if EF = 1, Me is not enriched in the atmosphere, which implies a crustal source.

Enrichment factors have been calculated for several metals in different localities by Lantzy and Mackenzie (1979), Duce et al. (1975), Chester and Stoner (1974), and Zoller et al. (1974). A summary of these studies shows that Se, Pb, Sb, Cd, Cu, and Zn have greater concentrations in the atmosphere in remote areas than would be expected from the contribution of crustal material; Co, Mn, Cr, and V showed relatively little or no enrichment (Figure I-1).

In remote areas (e.g., Antarctica, the South Atlantic Ocean) there is some question as to the causes of EF > 1 (Duce et al. 1975). Possible reasons, other than the long-range transport of anthropogenic aerosols, could be high-temperature volatilization

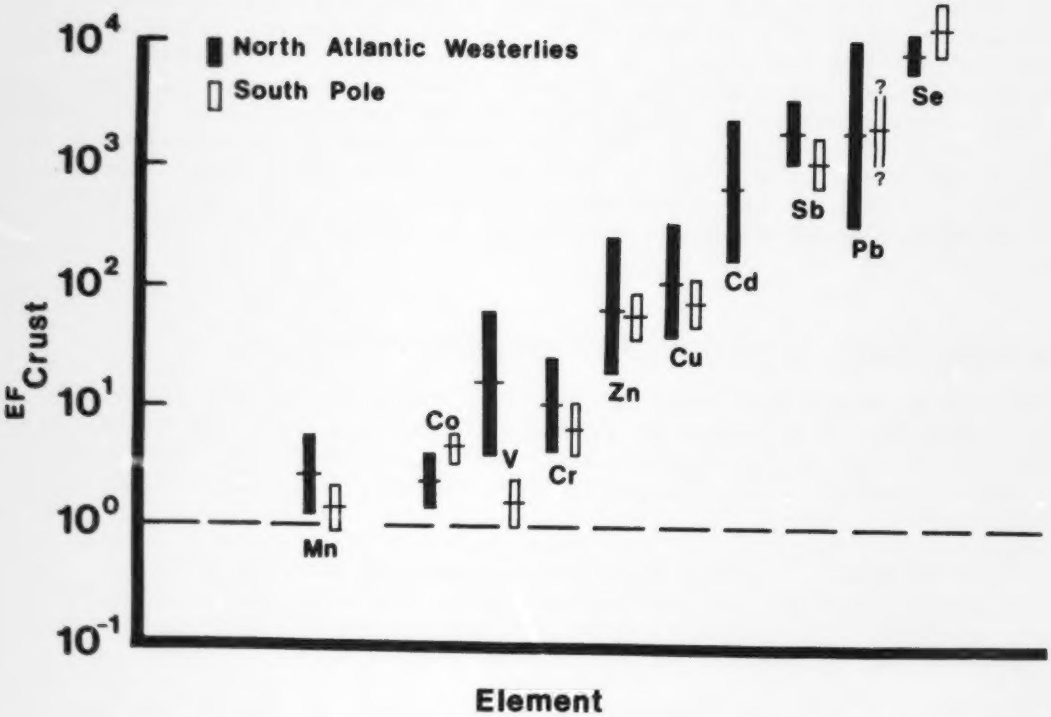


Figure I-1. EF_{crust} values for atmospheric trace metals collected in the North Atlantic westerlies from R/V Trident, Bermuda, and at the South Pole. The vertical bars represent the geometric standard deviation; the horizontal dashes (crossing the bars), the geometric mean-enrichment factor (Duce et al. 1975, p. 60; copyright 1975 by the American Association for the Advancement of Science.)

(volcanoes), low-temperature volatilization, or improper reference material. For example, since Se is emitted into the atmosphere in the vapor phase as well as by injection of crustal material, the EF ratio may be artifically large. The same may be true of Hg and As, although their EF values have not been calculated.

In densely populated areas of the United States, anthropogenic activity probably causes EF > 10. For example, natural emissions of sulfur are about 1.3 times greater than anthropogenic emissions, on a global basis. However, because of the intensity of anthropogenic emissions in the eastern United States, the ratio of anthropogenic to natural emissions is about 100 (Galloway and Whelpdale 1980). Therefore, for the United States, the relative order of the enrichment of metals in the atmosphere by anthropogenic processes is estimated to be Se > Pb > Sb > Cd > Cu, Zn > Cr > V > Co.

2.3. Determination of Historical Trends in Deposition

The third technique uses historical records on the composition of atmospheric deposition found in glaciers (Herron et al. 1977; Weiss et al. 1975) and in lake sediments from remote areas (Davis and Galloway 1980; Galloway and Likens 1979; Norton et al. 1978, 1980).

In the glacial records from Greenland, Zn and Pb have increasing rates of atmospheric deposition. But, as Boutron (1980) recently stated, the increasing rates are based on very few reliable analytical data even for these elements.

Most studies of mercury on the Greenland ice sheet can now be discounted because of erroneous sampling and analytical defects (McLean et al. 1980). A more recent study based on exceptionally careful analytical techniques showed no increase in mercury deposition in the ice sheet between 1727 and 1971 (Appelquist et al. 1978).

For some lake sediments in the eastern United States, large increases (>10 times) in the rates of deposition in the sediment are seen for Pb, Sb, and Au, with smaller increases (>5 times) for Ag, Cd, and Cu. Cr, Zn, and V show only slight increases (Figure I-2). These increases in sediment deposition are primarily caused by increases in atmospheric deposition (Galloway and Likens, 1979; Norton et al., 1978, 1980). The magnitude of the increases of the atmospheric deposition of metals depends partially on the location of the lake relative to the source. As an example, data on lead deposition from three lakes in the eastern United States are presented in Figure I-3. The three lakes lie on a line normal to the mean annual air flow (Figure I-4) and downwind from metropolitan areas that are sources for atmospheric lead.

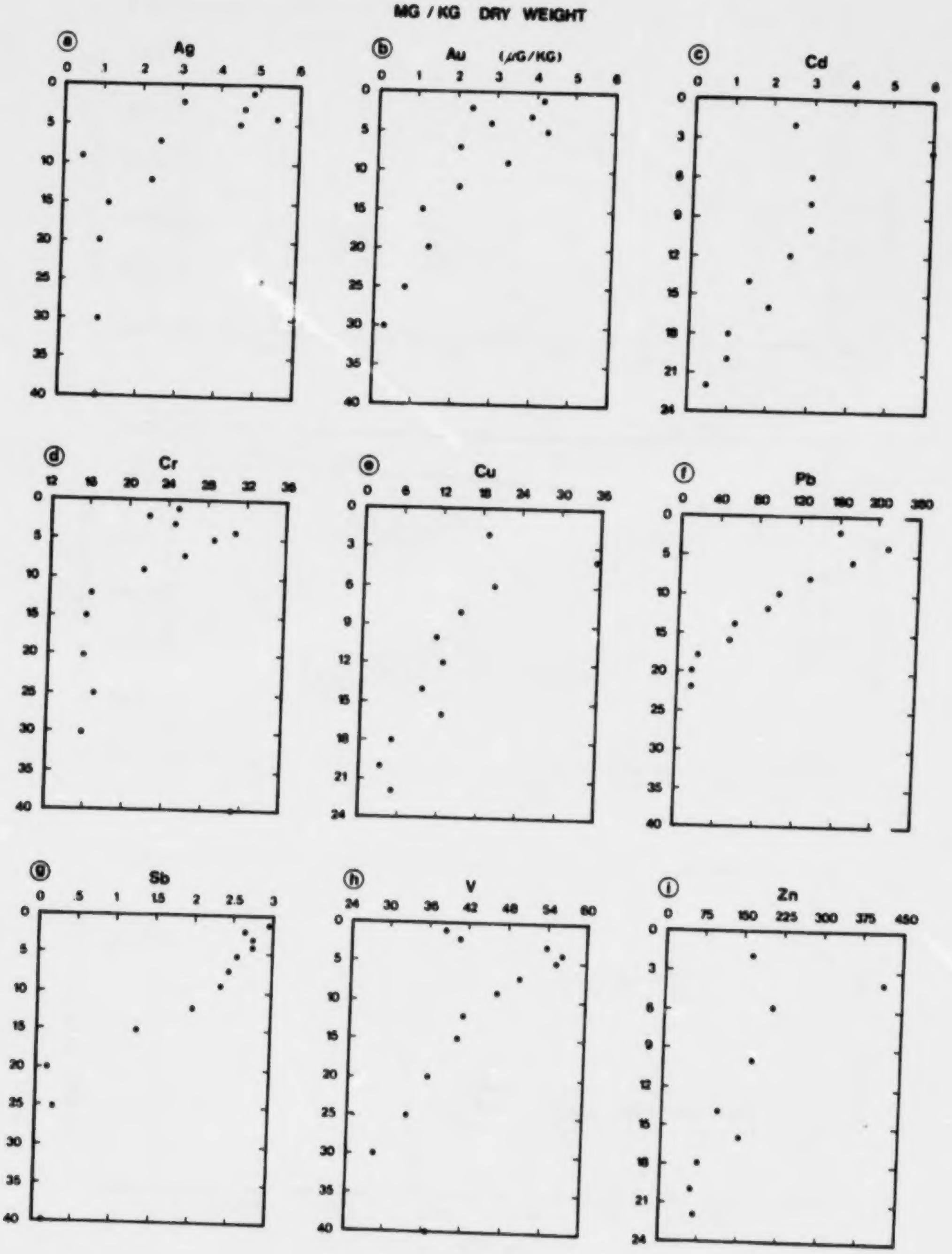


Figure I-2. Element concentrations versus depth in sediment of Woodhull Lake, New York. (Galloway and Likens 1979, p. 429; copyright 1979 by American Society of Limnology and Oceanography, Inc.)

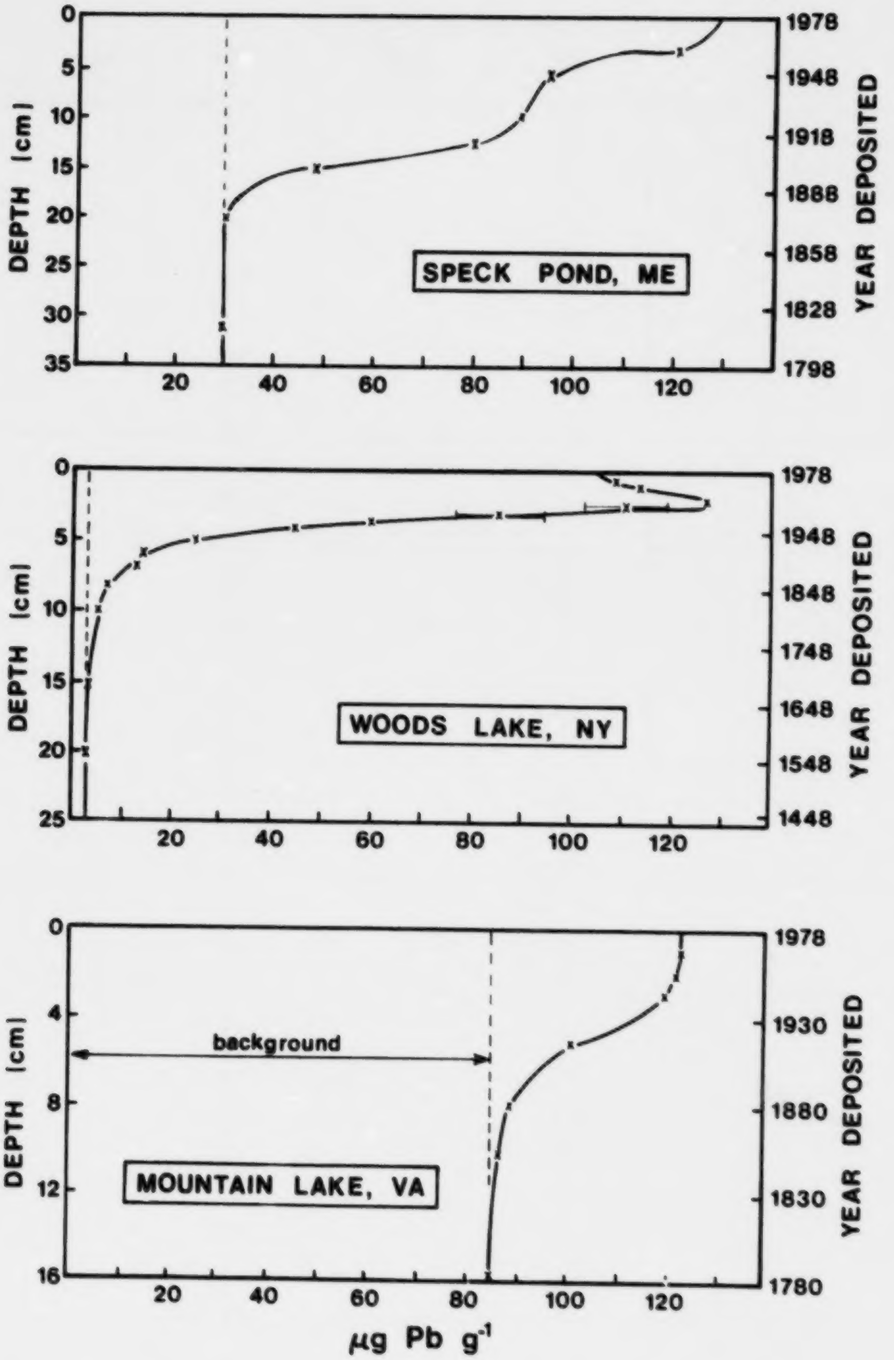


Figure I-3. Pb concentration as a function of depth in the sediments of three lakes. Year deposited is approximate and was determined by Pb^{210} and/or Cs^{137} dating. Locations of the lakes are shown in Figure I-4.

These profiles of lead deposition (Figure I-3) show that the Maine and New York lakes have accumulated more lead, relative to natural levels, than the Virginia lake. This is consistent with increases being due to atmospheric deposition; the lake in Virginia is less influenced by anthropogenic Pb sources because it is farther from those sources.

Although several studies have related the variation of mercury concentration with its depth in sediment cores to variations in the deposition rate, Matsunaga (1978) reported that diagenesis causes significant mercury movement in sediments. Therefore, sediment cores may not give as valid a measure of mercury deposition as they do of less mobile metals.

2.4 Comparison of the Three Techniques

The results of the first two techniques (Mobilization and Enrichment Factors) predict which metals in atmospheric deposition will be affected the most by anthropogenic processes. The third technique (historical trends in deposition) provides an actual measurement (primarily for areas of the eastern United States) of the metals that will be affected. A comparison of the relative rankings of all three techniques (Table I-2) shows a basic agreement on which metals should have the greatest degree of enrichment. For example, the predictions of the first two techniques, that Ag, Cd, Cu, Pb, Sb, Se, and Zn should have increased rates of atmospheric deposition, are supported by the analyses of temporal trends in atmospheric deposition for the metals Ag, Cd, Cu, Pb, Sb, V, and Zn.

It is noteworthy that the three techniques agree as well as they do since the predictions of the first two techniques rely on the assumption that the primary natural source in the eastern United States is the soil. However, since they do agree, it appears that, in the eastern United States at least, the rates of atmospheric deposition of Ag, Cd, Cu, Pb, Sb, V, and Zn are strongly influenced if not controlled by anthropogenic processes.

Unfortunately, there are many metals for which we do not have adequate data, i.e., As, Be, Co, Cr, Hg, Mn, Mo, Ni, Sn, Te, and Tl. To better understand the effects of anthropogenic processes on the cycling of these metals, their temporal trends of atmospheric concentration and deposition must be determined.

3. CONCENTRATION OF METALS IN THE ATMOSPHERE

The amount of a metal in either wet or dry deposition is directly related to the concentration of the metal in the atmosphere. Most metals are associated with particulate matter in the atmosphere and the concentrations are measured by collecting a

Table I-2. Three Techniques for Determining the Influence of Anthropogenic Processes on the Concentration of Metals in Atmospheric Deposition

Techniques	Expected Enrichment			
	Low	Moderate	Large	No Data
Mobilization factor*	Co, Mn, Hg	As, Cr, Ni, Se, V	Ag, Cd, Cu, Mo, Pb, Sb, Se, Sn, Zn	Be, Te, Tl
Enrichment factor	Co, Mn, Ni	Cr, V	Cd, Cu, Pb, Sb, Se, Zn	Ag, As, Be, Hg, Mo, Sn, Te, Tl
Historical factor	Co, Mn, Ni	Cr, Cd, V	Ag, Cu, Pb, Sb, Zn	As, Be, Hg, Mo, Se, Sn Te, Tl

NOTE: Low = <2 x enrichment; moderate = 2 to 5 x; and large = >5 x.

*The MF is based on the comparison of global emission rates. On a reduced scale, as for the United States, the relative order will change; for example, Hg, As, and Se would be expected to be in categories of higher enrichment.

known volume of air, using among others, filters, impactors, etc. For metals and their compounds existing in the gas phase, selective absorbents can be used for collection or direct determination can be made with atomic absorption following gas chromatography.

Many metal concentrations on atmospheric particulates have been determined and are presented in Appendix A. The data were classified into the following regions:

Remote -	Any areas of lowest concentration. There was a large discrepancy between data from the Antarctic and the Arctic (Norway, Greenland, Canada), with the latter having somewhat higher concentrations. Both sets of data have been included in the remote range until the discrepancy can be resolved.
Rural -	Any site not subject to the direct influence of local anthropogenic sources but representative of a regional background.
Urban -	Any site (in a city or elsewhere) subject to a local anthropogenic source.

When available, the first set of data for each element in each region was from Eisenreich et al. (1978). Reported concentrations for many elements varied widely, perhaps because of measuring errors. In addition, very few data have been reported for many toxic metals. For example, no remote data were available for Be or Sn and only Dams and deJonge (1976) reported remote values for Ag and Mo.

Ranges of these concentrations are summarized in Table I-3; median concentrations are given in Table I-4. For the remote sites, obvious outliers on the high end were omitted from the ranges in Table I-3.

As measurement techniques improve, a more accurate set of median remote concentrations for trace metals in the atmosphere will be devised. However, for the present, these median remote concentrations can be used to assess the effect of emission sources (natural or anthropogenic) on metal concentrations in the atmosphere.

Table I-5 gives the ratios of the median concentrations in the rural and urban areas to the median remote concentrations for each metal. This concentration factor for the rural areas compared with the remote areas showed that anthropogenic activity influences the concentration of metals in the atmosphere in the order of Zn > Pb > Mn > Cu, Ag, As > Sb, Se, Cr > Cd > Hg, Ni, V > Co. This order, based on a very uncritical examination of atmospheric metal concentrations, agrees with that in Tables I-2 and I-10, except for Mn and Cd. The anthropogenic contribution to the atmosphere was clearly highest for Zn and Pb, elements with widely dispersed emission sources.

A number of the other elements have similar rural/remote concentration ratios within a factor of two (Ag, As, Cr, Cu, Sb, Se). This could indicate common sources and similar atmospheric-transport characteristics. Although the low position of mercury may seem rather surprising, its high volatility may have caused it to be more widely dispersed. However, the state of the science is not adequate to distinguish anthropogenic from natural emissions of volatile elements (Hg, Se, As).

4. CONCENTRATION OF METALS IN WET DEPOSITION

The regional concentration of trace metals in atmospheric deposition cannot at present be quantitatively assessed because of the lack of a national atmospheric-deposition program for metals. However, some preliminary assessments can be made by using data from historical networks and compiling the work of several independent investigations of metals in atmospheric deposition in remote, rural, and urban areas.

Table I-3. Ranges of Metal Concentrations in the Atmosphere

Metal	Site	Range (ng m^{-3})
Ag	Remote	0.01
	Rural	0.3
	Urban	1.1
As	Remote	0.17 - 1.47
	Rural	0.31 - 12.1
	Urban	0.3 - 130
Be	Rural	0.023
	Urban	0.14
Cd	Remote	0.003 - 0.62
	Rural	0.07 - 1.96
	Urban	0.07 - 118
Co	Remote	0.0008 - 3
	Rural	0.04 - 2.0
	Urban	0.07 - 43
Cr	Remote	0.005 - 2
	Rural	0.22 - 65
	Urban	0.39 - 1100
Cu	Remote	0.024 - 10
	Rural	0.9 - 72
	Urban	0.12 - 4000
Hg	Remote	0.03 - 0.208
	Rural	0.02 - 4
	Urban	0.06 - 11.2
Mn	Remote	0.01 - 54
	Rural	1.1 - 647
	Urban	1.7 - 5400
Mo	Remote	0.01 - 54
	Urban	<1 - 3.4
Ni	Remote	0.35 - 3
	Rural	1.3 - 50
	Urban	0.2 - 1000
Pb	Remote	0.1 - 64
	Rural	0.6 - 451
	Urban	0.8 - 8300
Sb	Remote	0.05 - 0.64
	Rural	0.18 - 7
	Urban	12 - 43
Se	Remote	0.042 - 0.40
	Rural	0.09 - 3.3
	Urban	4.7
Sn	Rural	55
	Urban	99
V	Remote	0.0015 - 14
	Rural	0.37 - 15
	Urban	2.8 - 600
Zn	Remote	0.03 - 31
	Rural	3.8 - 1200
	Urban	0.3 - 3120

NOTE: For comparative purposes, where ranges were not available single values were used.

Table I-4. Approximate Median Concentrations of Metals in the Atmosphere (ng m^{-3})

Metal	Remote	Rural	Urban
Ag	0.01	0.3	1.1
As	0.2	6	25
Be	--	0.023	0.14
Cd	0.1	1.0	2.0
Co	0.05	0.1	10.0
Cr	0.3	5.0	40.0
Cu	0.2	6.0	100
Hg*	0.5	2.0	20
Mn	0.4	30.0	150
Mo	0.3	--	2
Ni	0.36	2	30
Pb	1.0	100	2000
Sb	0.2	3	30
Se	0.1	1.5	4.7
V	1.0	5	50
Zn	0.5	100	1000

*Total Hg in atmospheric measurement.

Table I-5. Ratios of Median Concentrations of Metals in the Atmosphere

Metal	Urban/Remote	Rural/Remote
Ag	110	30
As	125	30
Cd	20	10
Co	200	2
Cr	133	17
Cu	500	30
Hg	40	4
Mn	375	75
Mo	7	--
Ni	83	6
Pb	2000	100
Sb	150	15
Se	47	15
V	50	5
Zn	2000	200

Data from a 32-station national network operating during parts of 1966 and 1967 (Lazrus et al. 1970) show distinct maxima in Pb and Zn deposition east of the Mississippi River (Figures I-5 and I-6). The high rate was caused by the large amount of fossil fuel used in the eastern United States and transport by the prevailing easterly winds (Figure I-4). It also caused the increased deposition of Pb and Zn found in sediments of remote lakes in the area (Figure I-2).

Because of the lack of systematically collected data for other metals, the results of many different investigations of metal concentrations in wet deposition have been stratified into three categories in Appendix B: remote, rural, and urban areas. This compilation shows how few data are available for most metals and how few toxic metals have ever been studied. No studies have measured Be, Sb, Sn, Te, and Tl and fewer than fifteen studies have measured Ag, As, Co, Cr, Se, and V.

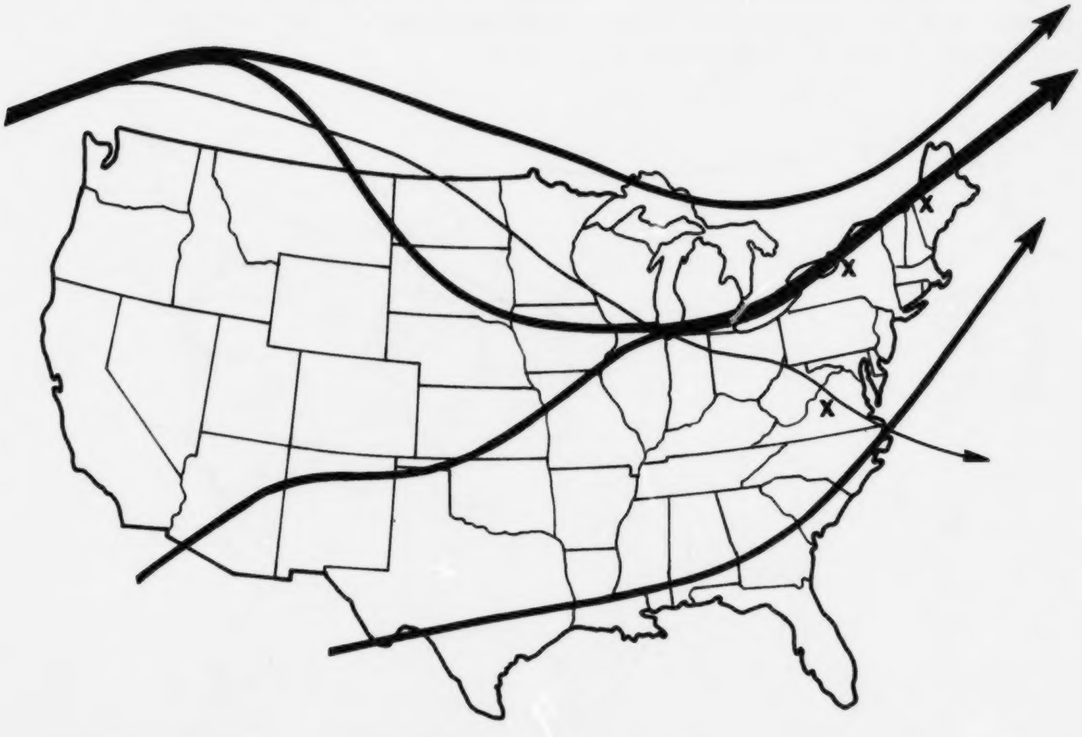


Figure I-4. Airflow over the United States; X refers to locations of lakes in Figures I-2 and I-3; thickness of airflow lines indicates degree of prevalence (data from Van Cleef 1908).

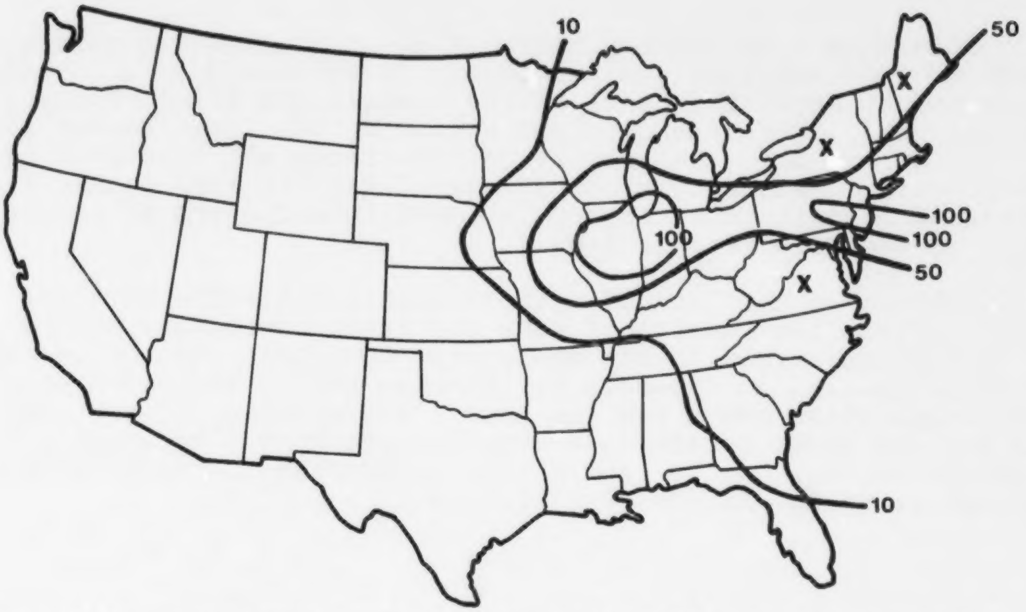


Figure I-5. Average deposition (g ha^{-1} mo^{-1}) of Pb by precipitation from September 1966 to March 1967 as determined by Lazrus et al. (1970). X refers to locations of lakes in Figure I-3 (Davis and Galloway 1980, with permission of the copyright holder, Ann Arbor Science Publishers, Inc.).

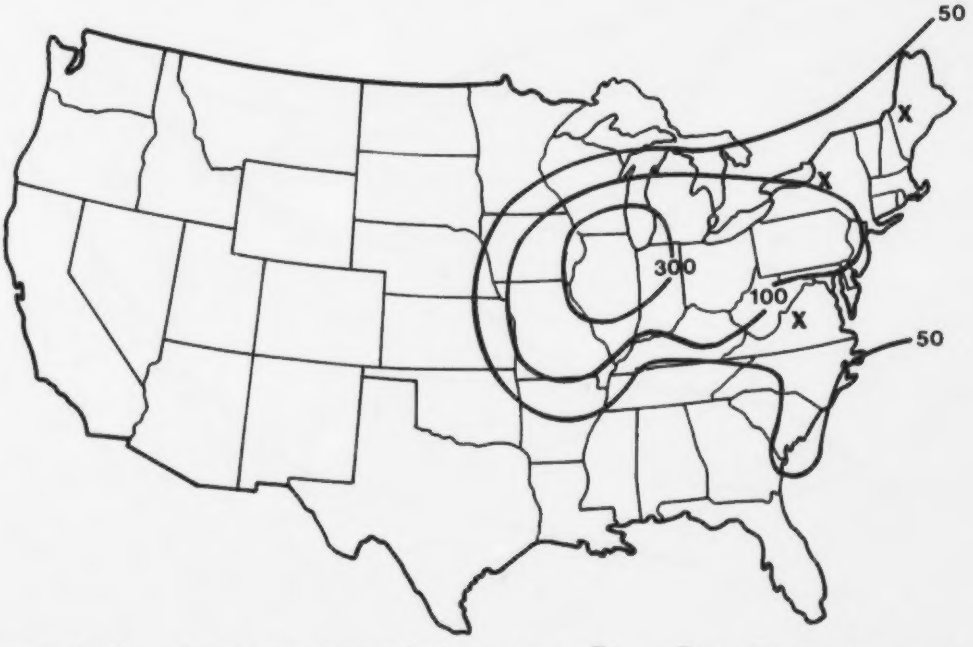


Figure I-6. Average deposition (g ha^{-1} mo^{-1}) of Zn by precipitation from September 1966 to March 1967 as determined by Lazrus et al. (1970). X refers to locations of lakes in Figure I-3 (Davis and Galloway 1980, with permission of the copyright holder, Ann Arbor Science Publishers, Inc.).

The ranges of metal concentrations in precipitation varied widely within these three categories--up to four orders of magnitude for some metals--reflecting the different methods of sampling and analyses and the many different locations. For example:

(1) Observation periods range from as short as one month to as long as two years.
(2) Collection frequencies range from event sampling to monthly and to even yearly sampling.
(3) Collector designs are different.
(4) Samples are treated differently (e.g., filtered vs. unfiltered).
(5) Analytical methods vary considerably.
(6) Distinctions between remote, rural, and urban sites are subjective, particularly between rural and urban sites.

Because of these differences in sampling techniques, the lack of data, and the wide variations in concentrations, it is difficult to assign a representative concentration value for any given metal in any given area.

With this realization, the data-analysis approach used previously for metal concentrations in the atmosphere was also used for metal concentrations in wet deposition. Ranges of metal concentrations were calculated for remote, rural, and urban precipitation (Table 1-6). For the urban and rural sites, all available data were included. It was assumed that within an urban environment extremely high and low concentrations are possible because of the concentration of sources. Most remote studies took place at either of the two poles and Greenland. Concentrations of metals at these locations are now thought to be lower than previously believed because of possible sample contamination. Therefore, older data were excluded when they were not considered representative of remote environments.

The median concentrations of metals in wet deposition are consistently higher for urban and lower for remote sites (Table I-7). However, because of the wide concentration ranges and lack of data (Table I-6), caution must be exercised if these data are used as typical of an urban, rural, or remote area.

Table I-6. Ranges of Metal Concentrations in Wet Deposition (Rain, Snow, and Ice)

Metal	Site	Range ($\mu g\ \ell^{-1}$)	No. of Refs.	Metal	Site	Range ($\mu g\ \ell^{-1}$)	No. of Refs.
Ag	Remote	0.006-0.01	2	Mn	Remote	0.018-	6
	Rural	0.023-0.48	7		Rural	0.1-4	19
	Urban	3.2	1		Urban	1.9-8	7
As	Remote	0.01	1	Mo	Urban	0.20	1
	Rural	<0.1-0.5	2				
Cd	Remote	0.004-0.639	7	Ni	Remote	<0.1	1
	Rural	0.08-0.5	17		Rural	0.6-2	9
	Urban	0.5-2.3	3		Urban	2.4-11	3
Co	Rural	0.01-1.5	2	Pb	Remote	0.02-.	7
	Urban	1.8	1		Rural	0.6-6	24
					Urban	5.4-14	6
Cr	Rural	0.1-<5	7	Sb	Remote	0.034	1
	Urban	0.51-1	3				
Cu	Remote	0.035-0.851	6	V	Remote	0.016-0.3	3
	Rural	0.4-3	22		Rural	0.13-7	3
	Urban	6.8-10	5		Urban	68	1
Hg	Remote	0.011-0.429	4	Zn	Remote	0.001-1	8
	Rural	0.01-0.2	7		Rural	1-31	25
	Urban	0.002-4.0	6		Urban	200-28	6

NOTE: For comparative purposes, where ranges were not available, single values were used. No data were found in the literature for Be, Se, Sn, Te, or Tl; Co, remote; Mo, remote, rural; Sb, rural, urban; Cr, remote. Only bulk values were found for Se and for As, urban.

Table I-7. Median Concentrations of Metals in Wet Deposition (Rain, Snow, and Ice) ($\mu g\ \ell^{-1}$)

Metal	Remote	Rural	Urban
Ag	0.008	0.040	3.2
As	0.019	0.5	--
Cd	0.008	0.6	0.7
Co	--	0.01	1.8
Cr	--	0.27	3.6
Cu	0.055	5.3	30
Hg	0.048	0.11	1.0
Mn	0.22	10.0	25
Mo	--	--	0.2
Ni	<0.1	1.5	17
Pb	0.14	15	41
Sb	0.034	--	--
V	0.022	1.1	68
Zn	0.22	45	40

NOTE: If only one concentration was available, it was used. If the median value was reported as a range, the middle of the range was used. If the median fell between two numbers, the lowest was used. If the median value was reported as a "less than" value, the next lowest was used. Insufficient data existed for Be, Se, Sn, Te, and Tl.

To assess how human activities have affected precipitation, the ratios of median metal concentrations in the urban and rural studies to those in the remote studies were calculated where possible (Table I-8). In rural areas, the toxic metals most affected by human activities were Zn > Pb > Cu > Cd > V > Mn > As > Ni > Ag > Hg. Except for Ag, this agees well with the predictions (Table I-2). And except for Cd and V, it also agrees well with the analysis of the effect of anthropogenic activities on metal concentrations in the atmosphere in rural relative to remote areas.

The low ratio for Hg was almost certainly due to its wide distribution (see above) and the inefficient scavenging of the predominantly vapor species in precipitation. Insufficient data existed for Be, Co, Cr, Mo, Sb, Se, Sn, Te and Tl to make any calculations.

Table I-8. Ratios of Median Concentrations of Metals in Wet Deposition (Rain, Snow, and Ice)

Metal	Urban/Remote	Rural/Remote
Ag	400	5
As	--	26
Cd	87	75
Cu	554	96
Hg	21	2
Mn	113	45
Ni	170	15
Pb	292	110
V	3090	50
Zn	181	200

NOTE: Insufficient data existed for Be, Co, Cr, Mo, Sb, Se, Sn, Te, and Tl.

5. DEPOSITION OF METALS FROM THE ATMOSPHERE

5.1 Deposition in Remote, Rural, and Urban Environments

Our present knowledge of the deposition rate of toxic metals is very primitive; it is comparable with our knowledge of major cations (H, Na, K, Mg, Ca) in precipitation twenty years ago. This is due partially to the inability, until recently, to quantitatively analyze constituents in water at the microgram per liter level or less and partially to an ignorance of the potential significance of this deposition.

Table I-9 presents data selected from the literature available on deposition rates of toxic metals. These data vary in quality and are not strictly comparable for the same reasons stated for metal concentrations in wet deposition. In addition, because of the lack of data and the effect that annual precipitation amounts have on total deposition, a relative ordering of these metals most influenced by anthropogenic activities is not possible.

However, even given these constraints certain general conclusions can be drawn.

(1) Remote: Values reported for metals deposited in Antarctica were generally an order of magnitude lower (Boutron 1979a,b) than those reported in Greenland (Boutron 1979c), which in turn were an order of magnitude lower than those reported from North Atlantic precipitation (Duce et al. 1976).

(2) Rural: Values reported for metals deposited over rural areas were from 10 to 10^2 times higher than those from North Atlantic precipitation.

(3) Urban: Values reported for metals deposited over urban areas were from 10^2 times to 10^4 times higher than those from North Atlantic precipitation and up to 10^6 times higher than those from Antarctica.

5.2 The Relative Importance of Dry versus Wet Deposition

Most data in Table I-9 are for bulk deposition, which is a combination of dry and wet. In terms of our understanding of atmospheric processes and our assessment of the effects of toxic-metal deposition, it is important to know the relative contributions of each.

Actual measurements of toxic metals in deposition suggest that the fraction deposited dry is substantial. Few cases in the literature have indicated that the dry fraction is less than 0.1 of the total deposit. For the most part, the mean dry fraction lies between 0.3 and 0.6. Table I-10 summarizes data for several

Table I-9. Selected Values of Atmospheric-Deposition Rates for Metals in Remote, Rural, and Urban Areas

		Precipitation	kg ha^{-1} yr^{-1}	Reference
Ag				
	Remote	Bulk	2.1×10^{-6}	Boutron 1979b
			2.7×10^{-5}	Ibid.
	Rural	Bulk	$<1 \times 10^{-2}$	Cawse 1977
			3.4×10^{-4}	Struempler 1976
As				
	Remote	Bulk	3.1×10^{-4}	Duce et al. 1976
	Rural	Dry	$<3.6 \times 10^{-3}$	U.S.DOE 1979
		Wet	$<8.0 \times 10^{-1}$	Ibid.
		Bulk	2×10^{-2}	Dethier 1977
			0.01 - 0.50	Cawse 1977
			<10.15	U.S.DOE 1979
	Urban	Dry	$<3 \times 10^{-3}$	Ibid.
		Wet	<1.23	Ibid.
		Bulk	<1.14	Ibid.
			$2.5\text{-}6 \times 10^{-2}$	Dethier 1977
Cd				
	Remote	Bulk	5×10^{-5}	Weiss et al. 1975
			2.3×10^{-6}	Boutron 1979b
			3.7×10^{-5}	Ibid.
	Rural	Dry	$<4.7 \times 10^{-2}$	U.S.DOE 1979
		Wet	$<9.4 \times 10^{-2}$	Ibid.
		Bulk	<0.1	Cawse 1977
			$<2.4\text{-}7.7 \times 10^{-3}$	Peyton et al. 1976
			4.0×10^{-3}	Vermeulen 1977; Semb 1978
			1.2×10^{-3}	Struempler 1976
			8.8×10^{-3}	Schlesinger et al. 1974
	Urban	Dry	$<9.4 \times 10^{-2}$	U.S.DOE 1979
		Wet	$<1.7 \times 10^{-1}$	Ibid.
		Bulk	$<1.3 \times 10^{-1}$	Ibid.
			$8.3\text{-}36 \times 10^{-3}$	Peyton et al. 1976
			7×10^{-3}	Vermeulen 1977
			2.6×10^{-1}	Peirson et al. 1973
Co				
	Rural	Bulk	<1.0	Cawse 1977
Cr				
	Remote	Bulk	3×10^{-3}	Duce et al. 1976
	Rural	Dry	$<2.0 \times 10^{-2}$	U.S.DOE 1979
		Wet	<0.57	Ibid.

Table I-9. (continued)

	Precipitation		$\text{kg ha}^{-1}\text{ yr}^{-1}$	Reference
Cr (continued)				
		Bulk	0.21	Ibid.
			10^{-2} - 0.5	Cawse 1977
			0.36	Andren and Lindberg 1977
	Urban	Dry	0.4	U.S.DOE 1979
		Wet	<0.7	Ibid.
		Bulk	10.6	Ibid.
Cu				
	Remote	Bulk	7.0×10^{-4}	Weiss et al. 1975
			1.9×10^{-3}	Duce et al. 1976
			1.2×10^{-5}	Boutron 1979b
			1.9×10^{-4}	Ibid.
	Rural	Bulk	1.8×10^{-2}	Struempler 1976
			0.23	Andren and Lindberg 1977
			0.12	Dethier 1977
			3.6×10^{-2}	Biggs 1979 (Personal communication to S.A. Norton)
			0.01 - 0.5	Cawse 1977
			5×10^{-2}	Vermeulen 1977
			0.1	Lazrus et al. 1970
			7.4×10^{-2}	Semb 1978
	Urban	Bulk	0.16 - 0.32	Dethier 1977
			0.168	Vermeulen 1977
			0.6	Lazrus et al. 1970
Hg				
	Remote	Dry	$>2.0 \times 10^{-2}$	Siegel and Siegel 1978
		Bulk	2×10^{-4}	Weiss et al. 1975
	Rural		7.3×10^{-4}	Schlesinger et al. 1974
			3.2×10^{-3}	Andren and Lindberg 1977
			1×10^{-2}	Cawse 1977
	Urban	Bulk	1.5×10^{-2}	Lockeretz 1974
Mn				
	Remote	Bulk	6.2×10^{-3}	Duce et al. 1976
	Rural	Dry	<0.31	U.S.DOE 1979
		Wet	<0.25	Ibid.
		Bulk	<0.29	Ibid.
			2.1×10^{-2}	Struempler 1976
			0.25	Andren and Lindberg 1977
			0.01 - 0.5	Cawse 1977
	Urban	Dry	<0.83	U.S.DOE 1979
		Wet	<0.99	Ibid.
		Bulk	<1.00	Ibid.

Table I-9. (continued)

		Precipitation	kg ha^{-1} yr^{-1}	Reference
Mo	Rural	Bulk	$<10^{-2}$	Cawse 1977
Ni	Rural	Dry	0.09	U.S.DOE 1979
		Wet	<0.87	Ibid.
		Bulk	<0.23	Ibid.
			0.01 - 0.5	Cawse 1977
			10^{-2}	Lazrus et al. 1970
	Urban	Dry	<1.1	U.S.DOE 1979
		Wet	<2.74	Ibid.
		Bulk	<2.24	Ibid.
			0.1	Lazrus et al. 1970
Pb	Remote	Bulk	9.3×10^{-3}	Duce et al. 1976
			1.2×10^{-5}	Boutron 1979b
			7.85×10^{-4}	Ibid.
	Rural	Dry	<0.72	U.S.DOE 1979
		Wet	<2.1	Ibid.
		Bulk	<2.72	Ibid.
			1.9×10^{-2}	Struempler 1976
			0.20	Schlesinger et al. 1974
			0.246	Andren and Lindberg 1977
			0.16	Dethier 1977
			6.2×10^{-2}	Biggs 1979 (Personal communication to S. A. Norton)
			0.32	Siccama and Smith 1978
			0.01 - 0.5 (filtered)	Cawse 1977
			0.048 - 0.216	Peyton et al. 1976
			0.226	Vermeulen 1977
			6×10^{-2}	Lazrus et al. 1970
			0.17	Semb 1978
	Urban	Dry	<2.97	U.S.DOE 1979
		Wet	<26.5	Ibid.
		Bulk	12.36	Ibid.
			0.1	Coello et al. 1974
			0.21	Dethier 1977
			0.70	Dethier 1977
			0.89 - 2.11	Peyton et al. 1976
			2.15	Page and Ganje 1970
			0.37	Vermeulen 1977
			1.2	Lazrus et al. 1970

Table I-9. (continued)

		Precipitation	kg ha^{-1} yr^{-1}	Reference
Sb				
	Remote	Bulk	1.6×10^{-4}	Duce et al. 1976
	Rural	Bulk	$<10^{-2}$	Cawse 1977
Se				
	Rural	Bulk	$<10^{-2}$	Cawse 1977
V				
	Rural	Dry	<0.25	U.S.DOE 1979
		Wet	<4.8	Ibid.
		Bulk	12.4	Ibid.
			0.01 - 0.5	Cawse 1977
			3.6×10^{-2}	Vermeulen 1977
	Urban	Dry	<0.35	U.S.DOE 1979
		Wet	<9.04	Ibid.
		Bulk	8.3	Ibid.
			0.043	Vermeulen 1977
Zn				
	Remote	Bulk	1.1×10^{-5}	Boutron 1979b
			1.0×10^{-3}	Ibid.
			2.5×10^{-2}	Duce et al. 1976
	Rural	Dry	<2.02	U.S.DOE 1979
		Wet	<7.92	Ibid.
		Bulk	11	Ibid.
			4×10^{-2}	Struempler 1976
			0.50	Andren and Lindberg 1977
			0.06 - 0.17	Dethier 1977
			0.5 - 10.0	Cawse 1977
			0.29 - 0.97	Peyton et al. 1976
			0.82	Vermeulen 1977
			0.2	Lazrus et al. 1970
			0.4	Semb 1978
	Urban	Dry	<5.94	U.S.DOE 1979
		Wet	<11.9	Ibid.
		Bulk	15.8	Ibid.
			0.35	Dethier 1977
			1.57 - 4.81	Peyton et al. 1976
			1.9	Vermeulen 1977
			3.6	Lazrus et al. 1970

NOTE: No data available on the elements Be, Sn, Te, Tl.

Table I-10. Means of Data Reported from All Seasons for Dry Fraction of Total Deposition

Metal	Reported Measurement of Dry Fraction		
	Marine	Rural	Urban
As	---	---	0.2
Cd	0.4	0.4	0.6
Cu	0.5	---	---
Mn	0.5	0.5	0.5
Ni	0.6	0.5	0.5
Pb	0.6	0.3	0.2
V	0.4	---	---
Zn	0.7	0.4	0.5

SOURCE: Values for the marine environment from Duce (1979); for rural and urban areas from Feely and Larsen (1979); data for Ag, Be, Co, Cr, Hg, Mo, Sb, Se, Sn, Te, and Tl were not included.

toxic metals in deposition from marine, rural, and urban areas. No systematic trend between the different environments is evident; the median value of all of the data is 0.5.

5.3 Physical Characteristics of Metals and Their Compounds Affecting Atmospheric Deposition

The physical characteristics of a metal and its compounds (particle size, vapor pressure, solubility, heats of solution, etc.) largely determine the type of deposition process. Eventually knowing what species of metal is present in the atmosphere and its physical properties, particularly the vapor pressure, particle size, and solubility, will enable rates of metal deposition to be predicted.

5.3.1. Vapor Pressure

In contrast to organic compounds (Part II), only a few metals in the atmosphere are in the vapor phase, as seen from an examination of the vapor pressures of the elements and their common oxides (Table I-11). Of all the elements, only mercury (Hg)

Table I-11. Vapor Pressures and Boiling Points of Metals and Their Common Oxides

Element	Boiling point (°C)	Vapor pressure at 500 K (mm Hg)	Vapor pressure at 1000 K (mm Hg)	Oxide	Boiling point (°C)	Vapor pressure at 500 K (mm Hg)	Vapor pressure at 1000 K (mm Hg)
Ag	2240	--	4.56×10^{-6}	--	--	--	--
As	613	6.27×10^{-4}	>400	As_2O_3	457	1.9×10^{-9}	--
				As_2O_5	(d 315)	6.3×10^{-7}	--
Be	2970	--	3.27×10^{-8}	BeO	3900	3.9×10^{-115}	3.9 x 10[illegible]
Cd	765	1.51×10^{-3}	466	CdO	1559	3.3×10^{-37}	9.0×10^{-4}
Co	2900	--	2.77×10^{-8}	CoO	>2000	--	--
Cr	2482	--	1.57×10^{-10}	Cr_2O_3	4000	--	--
Cu	2595	--	1.03×10^{-8}	Cu_2O	1800	--	--
				CuO	--	--	1.53×10^{-4}
Hg	356.58	44.2	--	HgO	(d 500)	--	--
Mn	2097	--	1.53×10^{-5}	MnO	2600	--	--
Mo	5560	--	$<1.9 \times 10^{-10}$	MoO_3	1155(s)	1.62×10^{-36}	0.22
Ni	2732	--	9.36×10^{-8}	NiO	>2000	1.3×10^{-72}	6.46×10^{-14}
Pb	1744	$< 3 \times 10^{-9}$	1.11×10^{-2}	PbO	>600	1.58×10^{-35}	4.5×10^{-3}
				PbO_2	(d 290)	--	--
Sb	1380	1.56×10^{-10}	7.46×10^{-1}	Sb_2O_3	1550	--	--
				Sb_2O_5	(d-0.380)	--	--
Se	685	7.8×10^{-3}	>400	SeO	180	--	--
				SeO_2	(d 340-350)	1.7×10^{-7}	--
				SeO_3	(d 180)	6.35 (400 K)	--
Sn	2270	--	5.0×10^{-8}	SnO	(d 1080^{600})	--	--
				SnO_2	1800	--	--
Te	999	1.65×10^{-6}	45.7	TeO_2	1245	1.1×10^{-32}	0.10
Tl	1457	1.66×10^{-10}	1.55×10^{-1}	Tl_2O	1865	--	--
				Tl_2O_3	875	--	--
V	3000	--	$<1 \times 10^{-10}$	V_2O_5	1750	--	--
Zn	907	2.61×10^{-5}	85.6	ZnO	(d 1975)	--	--

NOTE: d = decomposes; s = soluble

has a significant vapor pressure at ambient temperature (1.2 x 10^{-3} mm Hg at 20°C), and therefore its major deposition process will be dry deposition from the vapor phase. Based on vapor-pressure data at 500 K and 1000 K, the order of decreasing atmospheric concentration of the vapor phase of the elements is: Hg > Se > Cd > As > Zn > Te > Sb > Tl > Pb > Mn > Ag > Ni > Sn > Be > Co > Cu > Cr > Mo > V.

For the oxides, the order of decreasing vapor pressure (or increasing boiling point) is (SeO_3 > SeO_2) > (Ag_2O_5 > As_2O_3) > PbO > Tl_2O_3 > MoO_3 > TeO_2 > CdO, Sb_2O_3 > V_2O_5 > SnO_2 > Tl_2O > ZnO > Cu_2O > CoO, NiO, MnO > BeO > Cr_2O_3. Only the Se and As oxides have sufficient vapor pressure to have a significant proportion of the elements (if present as oxides) existing in the vapor phase in "clean" rural or remote air.

Therefore, from this analysis, only the metals Hg, Se, As, and perhaps Cd, could be expected to have a significant vapor-phase concentration relative to the total atmospheric concentration.

5.3.2 Particle Size

To estimate rates of both dry deposition and washout, or rainout, of toxic metals in particulate matter, it is necessary to have a knowledge of the particle-size distribution.

Particles in the atmosphere are commonly characterized by their "mass median diameter" (mmd): the particle size for which 50% of the mass occurs on larger and 50% on smaller particles. Some workers in the field of aerosol physics consider the mmd an oversimplification that essentially overlooks the fine structure of the mass versus particle size distribution. The urban aerosol, for instance, is often characterized by a bimodal particle-size distribution (e.g., Whitby et al. 1972; Whitby 1973; Bernstein and Rahn 1979). Rahn (1976) discussed this issue rather thoroughly, and concluded

> . . . it seems to be generally true that an element is unimodally formed in a particular size range of the aerosol, then remains there. Thus the mmd is a reasonable single-parameter description of the preferred particle size of an element in an aerosol.

Table I-12 summarizes mmd's for several toxic metals. The data are extremely scanty, and clearly more effort is required to determine size distribution of metals in different atmospheres.

Table I-12. Mass Median Diameter of Toxic Metals in Aerosols (μm)

Metal	Marine air	New York City	General (rural to urban)
Ag	--	<2.5	1
As	--	<2.5	1
Cd	0.5	<2.5	2
Co	--	--	4
Cr	--	<2.5	3
Cu	0.8	--	1.8
Hg	--	<2.5	0.5
Mn	0.4	<2.5	2
Mo	--	<2.5	1.2
Ni	--	<2.5	1.5
Pb	0.4	<2.5	0.4
Sb	--	<2.5	1
Se	--	<2.5	0.8
Sn	--	--	1.2
V	0.5	<2.5	1
Zn	--	<2.5	1.5

SOURCE: For marine-air values, Duce et al. (1979); for New York City, Bernstein and Rahn (1979); and for general (rural to urban), Rahn (1976).

NOTE: No data were found for Be, Te, or Tl.

5.3.3. Solubility

If we consider a hypothetical case, that atmospheric particles are either pure compounds or aerosol solutions of these, then the efficiency of absorption of the particle into the aerosol, and hence into cloud-water droplets, will increase with the solubility of the species. The efficiency of washout should therefore increase with the solubility of the species.

The solubilities of the four metal salts most likely to be present in atmospheric particulates are given in Table I-13. In most cases, because the solubility of the metal species is large relative to the amounts found in wet deposition, these compounds will dissolve in precipitation. However, since data on metal speciation in the atmosphere are limited, it is difficult to say that all metals will be found in their dissolved phase. Indeed, experimental data indicate that for some metals significant amounts are insoluble.

Also, in considering the dry deposition of pure compounds, deposition velocity varies with particle size (see Part III). Because of the minimum in this relationship, the most insoluble and the most soluble of the pure compounds have higher deposition velocities than those of intermediate solubility. The limits of this intermediate solubility have not yet been established.

Clearly to use the simplified deposition theory developed in Part III more fully and to evaluate the deposition of toxic metals, more detailed studies must determine the composition of the atmospheric particulates with which these metals are associated. Only then can rates of deposition be predicted.

5.4. Measurement of Wet Deposition

Collection techniques of samples for the analysis of major constituents in precipitation have been developed and standardized over the past few years (Galloway and Likens 1976, 1978; Berry et al. 1975; Granat 1976). Basically, these techniques use a collector that can be easily cleaned to eliminate contamination.

However, in the case of trace metals, new sampling and analytical problems are presented in their determination in dry deposition, rain, and snow. First, concentrations are much lower, generally ranging from 0.01 to 10 $\mu g\ \ell^{-1}$, thereby requiring more sensitive analytical methods and greatly increasing the potential for significant contamination. In addition, because of the low concentration and the properties of ionic metal species, adsorption of the metals onto the collector surface is a problem. Therefore, in any procedure for sampling precipitation for trace-metal analyses, the following precautions should be considered:

Table I-13. Solubility of Common Oxides, Sulfates, Chlorides, and Nitrates of Metals at 20°C*

Element	Species	Solubility† ($g\ \ell^{-1}$)		Species	Solubility† ($g\ \ell^{-1}$)	
		Oxide	Sulfate		Chloride	Nitrate
Ag	Ag_2X	0.013	5.7	AgX	0.00089	1220
As	As_2X_3	37	---	AsX_3	d	---
	As_2X_5	1500^{16}	---			
Be	BeX	0.0002^{30}	i	BeX_2	vs	vs
Cd	CdX	i	755	CdX_2	1680	1090
Co	CoX	i	362	CoX_2	450	---
Cr	CrX	i	123.5	CrX_2	vs	---
	Cr_2X_3	i	1200	CrX_3	i	s
Cu	CuX	i	143	CuX_2	706	1378
Hg	HgX	0.053	0.03^{16}	HgX_2	69	vs
Mn	MnX	i	520^{5}	MnX_2	723	4264
Mo	MoX	---	---	MoX_2	i	---
Ni	NiX	i	293	NiX_2	642	2385
Pb	PbX	0.017	0.043^{25}	PbX_2	9.9	377
Sb	Sb_2X_3	---	---	SbX_3	6016	d
Se	SeX_2	384^{14}	---	---	---	---
	SeX_3	vs	---	---	---	---
Sn	SnX	i	330^{25}	SnX_2	839	---
	SnX_2	i	vs	SnX_4	s	---
Te	TeX_2	d	---	TeX_2	d	---
Tl	Tl_2X_3	i	i	TlX	$2.9^{15.6}$	95.5
	Tl_2X	---	48.7	TlX_3	vs	s
V	V_2X_5	8	---	VX_2	d	---
Zn	ZnX	0.0016^{29}	965^{25}	ZnX_2	4320^{25}	3270^{40}

*Superscripts = solubility temperatures when not 20°C.

†i = insoluble, s = soluble, vs = very soluble, d = decomposes.

(1) Neither the collection vessel nor the structure should have metal surfaces.
(2) If the collector is automated, the motor assembly should be enclosed.
(3) The collection vessel should be washed in a clean room designed specifically for working with solutions with low trace-metal concentrations.
(4) The collection vessel should be acid washed and well rinsed; blanks of the washing and rinsing processes should be taken.
(5) After the precipitation has been collected, the sample should be acidified in the collection vessel to remove absorbed metals from the walls. This, however, will dissolve or desorb metals on particulate matter suspended in the sample.
(6) For the collection of precipitation to determine volatile metal species (e.g., Hg), the scavenging acid must be in the collection vessel before collection to prevent reemission. For Hg all vessels should be of glass and the scavenging acid be concentrated H_2SO_4 plus 5% $K_2Cr_2O_4$ (McLean et al. 1980).

Few interlaboratory, quality-control studies have been carried out on deposition samples collected for trace-metal analyses. Further evaluation studies are urgently needed.

5.5. Measurement of Dry Deposition

Several different devices have been designed, usually in the form of buckets or funnels (e.g., Volchok and Graveson 1976, Galloway and Likens 1976) to separate dry from wet deposition (historically to study fallout from nuclear-weapon tests).

These collectors all rely on artificial collection surfaces (plastic or metal), thus creating the basic question: how closely do artificial surfaces approximate natural ones such as water, grass, or leaves? Artificial surfaces are not completely satisfactory surrogates for "real-world" surfaces, particularly for studying the dry deposition of small particles and gases (e.g., Lundgren 1977; Slinn et al. 1979). However, Turekian et al. (1977), Pattenden (1977), and Volchok (1977; 1979, personal communication to S. Eisenreich) all found that quantitative data from their collections on artificial surfaces are at least partially accurate.

Another approach for determining the dry-deposition rate of metals is to measure atmospheric concentrations; then, using information on the phase of the metal, its solubility, its vapor pressure, and the type of receiving surface, calculate a deposition velocity. Both techniques have unique disadvantages. For a better understanding of trace-metal biogeochemical cycles, these difficulties must be resolved.

6. POTENTIAL EFFECTS OF INCREASES OF CONCENTRATION OF METALS IN ATMOSPHERIC DEPOSITION

High concentrations of metals deposited into lakes and streams, a common source of drinking water, can affect humans and other organisms by raising the levels of these metals above the acknowledged safety limits. The effect on other organisms is evident in water bodies (lakes, streams) with high metal concentrations due to atmospheric deposition.

6.1 Recommended Upper Limits in Water

Table I-14 lists the recommended upper limits that concentrations of metals should not exceed if man and other organisms are not to be affected. These are the minimum values quoted in the literature for reducing plant growth and for killing animals and plants.

Literature values, commonly site-specific, seldom evaluate such factors as the amount of biologically available toxic substance. For example, upper limits for Be range from 11 $\mu g\ \ell^{-1}$ (soft water) to 1100 $\mu g\ \ell^{-1}$ (hard water) and for cadmium, from 0.2 $\mu g\ \ell^{-1}$ (soft water) to 3.0 $\mu g\ \ell^{-1}$ (hard water). These ranges reflect the control of pH on greater complexing of various metals of higher pH (commonly associated with higher levels of dissolved anions). Also, organic ligands may ameliorate the effect of dissolved metals.

Of the metals for which there are limits, only Pb and Hg in precipitation approach the drinking-water standard as well as the limits for biological effects; the levels of Cd, Cu, Hg, Pb, and Zn in precipitation approach the limits for other biological effects (Figure I-7).

6.2 Metal Speciation in Relation to Toxicity

Metals in the atmosphere may be present as several species, with different levels of toxicity. We must, therefore, establish the speciation and how it relates to toxicity.

Little information on which metal species are present in the atmosphere and in precipitation is available. Several recent studies on the forms of mercury in the atmosphere have found that elemental mercury (>80%) is present although varying proportions of the more toxic methyl mercury species (0%-50%) have also been reported. (For reviews and evaluation of these studies, see Barton et al. 1980; Brouzes et al. 1980; McLean 1980; Matheson 1979.) Very few studies have been done on the gaseous forms of other metals (e.g., As and Se).

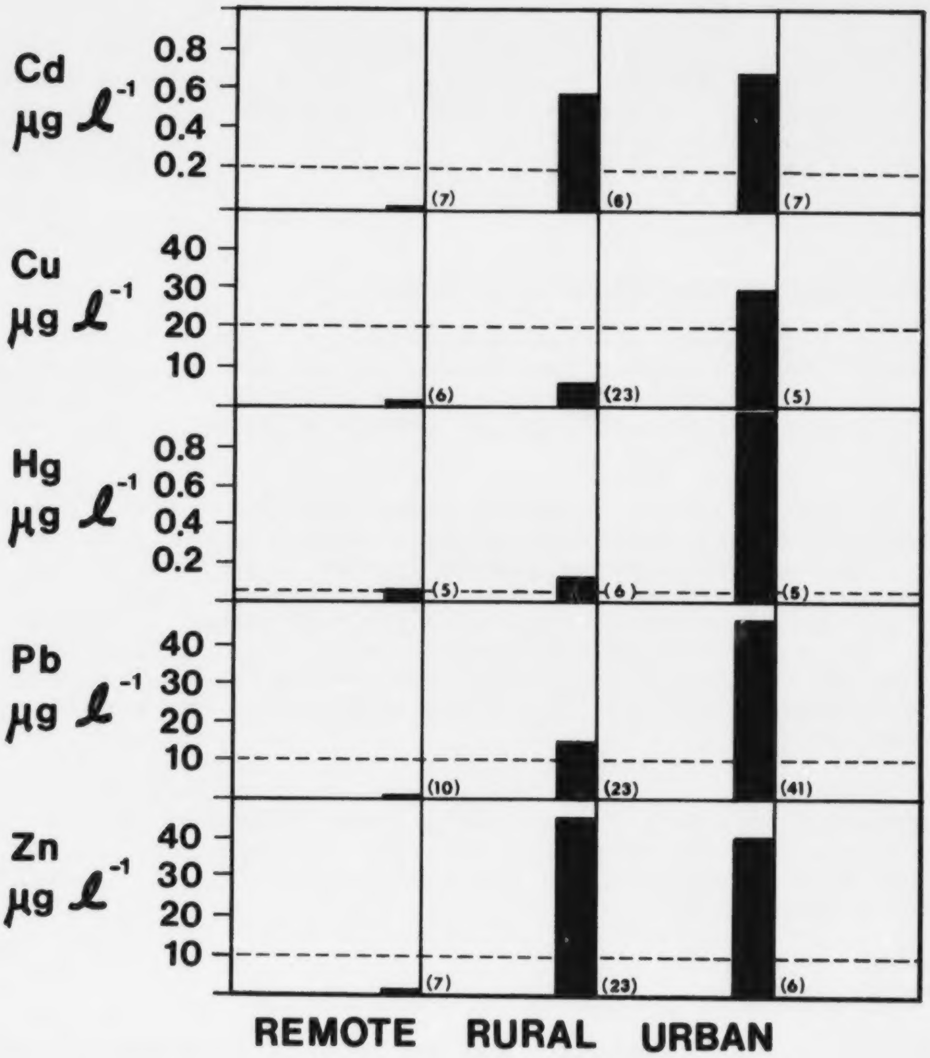


Figure I-7. Median concentrations of metals in precipitation in remote, rural, and urban areas relative to organism-toxicity levels.(---) denotes threshold of organism toxicity. Median values of metals in wet deposition are adapted from the data in Appendix B.

Table I-14. Recommended Upper Limits for Metal Concentrations in Water ($\mu g\ \ell^{-1}$)

Metal	Potable water	Organism toxicity
As	50	1.1*
Ag	50	no standard
Be	no standard	11.0
Cd	10	0.2
Co	no standard	0.1*
Cr	50	30.0
Cu	1000	20.0
Hg	2	0.05
Mn	50	1.0*
Ni	no standard	30.0
Pb	50	10.0
Se	10	500.0
Sn	no standard	>40.0
Tl	no standard	50.0
V	no standard	500.0
Zn	5*	100.0

SOURCE: For potable water values U.S.EPA (1976) and Torrey (1978); for organism toxicity values, Gough et al. (1979).

NOTE: No standard has yet been established for Mo, Sb, or Te.

*$mg\ \ell^{-1}$

For the metals in the atmosphere associated with particulate matter, almost no speciation has been carried out. However, most metals are likely to be associated with oxide, sulfide, sulfate, or nitrate.

Even fewer studies have been done on the species of metals present in precipitation than on those present in the atmosphere; however, elevated rates of methyl mercury have been found in snow close to an emission source (McLean 1980). To evaluate the effects of metals in atmospheric deposition, the data base on metal speciation must be improved.

7. SUMMARY

Information on nineteen metals in atmospheric deposition that are potentially toxic to humans and other organisms has been assimilated to determine if metal concentrations are increasing in atmospheric deposition and if these concentrations threaten human or organism health.

On the basis of rates of emission, atmospheric concentrations, and known temporal trends in deposition, the greatest increase in concentration of metals in atmospheric deposition due to anthropogenic activity are expected for Ag, Cd, Cu, Pb, Sb, Se, Zn, with smaller increases expected for Cr and V and with little or no increases expected for Co, Mn, and Ni. There were insufficient data to rank Mo, As, Be, Hg, Sn, Te, and Tl.

Although actual data on these metals in atmospheric deposition are limited, the data available supported these expectations. The metals Zn, Pb, Cu, Mn, Ag, As, and V had measured concentrations 30 to 200 times higher in atmospheric concentration or deposition in rural, continental areas than in remote areas such as the South Pole. Other metals, Sb, Se, Cr, and Ni, had concentrations that were 10 to 30 times greater in rural areas than in remote areas.

Metals can be deposited either wet or dry from the atmosphere. An assessment of the relative importance of these processes revealed that, depending on the metal and the area, dry deposition can be as great or greater a process than wet deposition.

On the basis of analyses of vapor pressures of metals and metal oxides, only Hg, As, Se, and, possibly, Cd could be expected to have a significant fraction of their atmospheric concentration in the vapor phase.

In regard to the effects of increased metal concentrations in atmospheric deposition, only Pb and Hg are currently in precipitation in some areas at levels greater than the drinking-water standard. Cd, Cu, Hg, Pb, and Zn can be present in precipitation at levels greater than the standards for effects on other organisms.

8. RESEARCH RECOMMENDATIONS

Although it was difficult to assimilate the work on metals in atmospheric deposition, the job was easier because so little has been done in spite of the scope of the problem. To avoid this in the future, we propose the following research recommendations:

(1) More data must be acquired through more studies, including the analysis of more metals.
(2) The concentration of soluble versus insoluble metals in rain and melted snow should be determined under the assumption that soluble metals are probably more mobile.
(3) Sampling and analytical methods must be standardized throughout the scientific community for all metals, including those that take on different forms in the atmosphere (i.e., Hg, As).
(4) Since dry deposition can be just as important as, if not more important than, wet deposition, standardized collection procedures must be developed.
(5) A detailed study of the metal compounds that predominate in rain and snow must be conducted.
(6) The size distribution of metals in urban, rural, and remote atmospheres needs to be determined.
(7) The fate of metals deposited into aquatic and terrestrial ecosystems must be determined.
(8) A national network to determine the temporal and spatial trends of metals in atmospheric deposition must be established.

9. REFERENCES

Andren AW, Lindberg SE, Bate LC. 1975. Atmospheric input and geochemical cycling of selected trace elements in the Walker Branch Watershed. Environ. Sci. Div. Pub. No. 728, Oak Ridge National Lab., Oak Ridge, TN.

Andren AW, Lindberg SE. 1977. Atmospheric input and origin of selected elements in Walker Branch Watershed, Oak Ridge, Tennessee. Water Air Soil Pollut. 8:199.

Appelquist HK, Jenson O, Sevel T. 1978. Mercury in the Greenland ice sheet. Nature 273:657.

Barton SC, Johnson ND, Christinson J. 1980. A study of atmospheric mercury deposition in Ontario. Ontario Research Foundation Report ΔP-2699/G-04 for the Minister of the Environment, Province of Ontario.

Beamish RJ, Van Loon JC. 1977. Precipitation loading of acid and heavy metals to a small acid lake near Sudbury, Ontario. J. Fish Res. Board Can. 34:649.

Bernstein DM, Rahn KA. 1979. New York summer aerosol study: Trace element concentrations as a function of particle size. New York Academy of Sciences Rep., NYA9-322-1-165, The New York Summer Aerosol Study.

Berry RL, Whelpdale DM, Wiebe HA. 1975. An evaluation of collectors for precipitation chemistry sampling. Rep. to WMO Expert Meeting on Wet and Dry Deposition, Downsview, Canada.

Biggs RB, Miller JC, Otley MJ, Shields CL. 1973. Trace metals in several Delaware watersheds. Rep. from Water Res. Center, University of Delaware, Newark.

Bogen J. 1974. Trace elements in precipitation and cloud water in the area of Heidelberg measured by instrumental neutron activation analysis. Atmos. Environ. 8:835.

Boutron C. 1979a. Alkali and alkaline earth enrichments in aerosols deposited in Antarctic snows. Atmos. Environ. 13:919.

_____. 1979b. Past and present day tropospheric fallout fluxes of Pb, Cd, Cu, Zn, and Ag in Antarctica and Greenland. Geophys. Res. Lett. 6:159.

_____. 1979c. Trace element content of Greenland snow along an east-west transect. Geochim. Cosmochim. Acta 43:1253.

_____. 1980. Trace metals in remote Arctic snows: Natural or anthropogenic. Nature 284:575.

Boutron C, Lorius C. 1979. Trace metals in Antarctic snows since 1914. Nature 277:551.

Brouzes RJP, McLean RAN, Farbas MO, McGraw SE, Tomlinson GH. 1980. Atmospheric input of mercury to natural waters. Atmospheric Input of Pollutants to Natural Waters, Eisenreich SJ, ed., Ann Arbor Science Pubs., Ann Arbor, MI (in press).

Carr RA, Wilkniss PE. 1973. Mercury in the Greenland ice sheet: Further data. Science 181:843.

Cawse PA. 1974. A survey of atmospheric trace elements in the United Kingdom (1972-73). Environmental and Medical Science Division, AERE Harwell Rep. R 7669, HMSO, London.

Cawse PA. 1977. Deposition of trace elements from the atmosphere in the U.K., Abstracts from Conference on Inorganic Pollution and Agriculture, Imperial College, London.

Chan KC, Cohen BL, Frohlinger JO, Shabason L. 1976. Pittsburgh rainwater analysis of P.I.X.E. Tellus 27:24.

Chester R, Stoner JH. 1974. The distribution of Mn, Fe, Cu, Ni, Co, Ga, Cr, V, Ba, Sr, Sn, Zn, and Pb in some soil-sized particulates from the lower troposphere over the world ocean. Mar. Chem. 2:157.

Coello WF, Saleem ZA, Kahn MAQ. 1974. Ecological effects of lead in auto exhaust. In: Survival in Toxic Environments, Kahn MAQ, Bederka JP, Jr., eds., Academic Press, New York.

Cooper HBH, Lopez JA. 1976. Chemical composition of acid precipitation in central Texas. Water Air Soil Pollut. 6:351.

Dams R, de Jonge J. 1976. Chemical composition of Swiss aerosols from the Jungfraujoch. Atmos. Environ. 10:1079.

Davis AO, Galloway JN. 1980. Atmospheric Zn and Pb deposition into lakes of the eastern United States. In: Atmospheric Input of Pollutants to Natural Waters, Eisenreich SJ, ed., Ann Arbor Science Pubs., Ann Arbor, MI (in press).

Dethier DP. 1977. Precipitation chemistry at an isolated site in the North Cascade range. Am. Geophys. Union Trans. 58:386.

Dickson W. 1975. The acidification of Swedish lakes. Rep. 54, Institute of Freshwater Research, Drottningholm, Sweden.

Drozdova VM, Makhonko EP. 1970. Content of trace elements in precipitation. J. Geophys. Res. 75:3610.

Duce RA. 1979. Pigeon key results. SEAREX Newsletter 2(4).

Duce RA, Hoffman GL, Zoller WH. 1975. Atmospheric trace metals at remote northern and southern hemispheric sites: Pollution or natural. Science 187:59-61 (10 January 1975).

Duce RA, Hoffman GL, Ray BJ, et al. 1976. Trace metals in the marine atmosphere: Sources and fluxes. In: Marine Pollutant Transfer, Windom H, Duce R, eds., Heath & Co., Lexington, MA.

Eisenreich SJ. 1980. Atmospheric input of trace metals to Lake Michigan. Water Air Soil Pollut. 13 (in press).

Eisenreich SJ, Hollod GL, Langevin S. 1978. Precipitation chemistry and atmospheric deposition of trace elements in northeastern Minnesota. Rep. to Minnesota Env. Quality Council.

Elgmork K, Hagen A, Langeland A. 1973. Polluted snow in southern Norway during the winters 1968-1971. Environ. Pollut. 4:41.

Evendijk JE. 1977. Trace metal content of atmospheric dust in Rotterdam. Paper presented at Fourth Annual Clear Air Congress, Tokyo.

Feely H, Larsen RJ. 1979. The chemical composition of atmospheric deposition. Environmental Measurements Lab Quarterly EML-363, Appendix.

Feely HW, Toonkel LE, Larsen RJ. 1979. Radio nuclides and trace metals in surface air. Environmental Measurements Lab Quarterly EML-367, C1.

Forland EJ, Gjessing YT. 1975. Snow contamination from washout/rainout and dry deposition. Atmos. Environ. 9:339.

Galloway JN, Likens GE. 1976. Calibration of collection procedures for the determination of precipitation chemistry. Water Air Soil Pollut. 6:241.

_____. 1978. The collection of precipitation for chemical analysis. Tellus 30:71.

_____. 1979. Atmospheric enhancement of metal deposition in Adirondack Lake sediment. Limnol. Oceanogr. 24:427.

Galloway JN, Whelpdale DM. 1980. An atmospheric sulfur budget for eastern North America. Atmos. Environ. 14:409.

Gatz DF. 1975. Pollutant aerosol deposition into southern Lake Michigan. Water Air Soil Pollut. 5:239.

Gjessing YT, Gjessing ET. 1973. Chemical composition of an Antarctic snow profile. Vatten 3:233.

Gough LP, Shacklette HT, Case AA. 1979. Element concentrations toxic to plants, animals and man. U.S. Geol. Surv. Bull. 1466:80.

Granat J. 1976. Principles in network design for precipitation chemistry measurements. J. Great Lakes Res. 2:42.

Hanssen JE, Ramback JP, Semb A, Steinues E. 1980. Atmospheric deposition of trace elements in Norway. International Conference of the Ecological Impact of Acid Precipitation. Sandefjord, Norway, March 11-14 (in press).

Harrison RM, Perry R, Wellings RA. 1975. Lead and cadmium in precipitation: Their contribution to pollution. J. Air Pollut. Control Assoc. 25:627.

Henriksen A. 1972. Quantitative chemical analysis of snow. Vatten 5:409.

Herron MM, Langway CC, Weiss HV, Cragin J. 1977. Atmospheric trace metals and sulfate in the Greenland ice sheet. Geochim. Cosmochim. Acta 41:415.

Herron MM. Langway CC, Weiss HV, Huxey P, Kerr R, Cragin J. 1976. Vanadium and other elements in Greenland ice cores. CRREL Rep. 76-24.

Hovmand MF. 1976. Deposition of metals from the atmosphere in Denmark. Institut for Okologisk Botanik, Copenhagen University.

Johannessen M, Henriksen A. 1978. Chemistry of snow meltwater: Changes in concentration during melting. Water Resour. Res. 14:615.

Jonasson IR. 1973. Migration of trace metals in snow. Nature 241:447.

Kennedy VC, Zellweger GW, Avanzino RJ. 1979. Variation of rain chemistry during storms at two sites in northern California. Water Resour. Res. 15:687.

King RB, Fordyce JS, Antoine AC, Leibecke HF, Neustadter HE, Sidik SM. 1976. Elemental composition of airborne particulates and source identification--An extensive one-year survey. J. Air Pollut. Control Assoc. 26:1073.

Konasewich D, Traversy W, Zar H. 1978. Organic and heavy metal contaminants in the Lakes Erie, Michigan, Huron and Superior basins. Status Report, Great Lakes Water Quality Board.

Kramer JR. 1973. Fate of atmospheric SO_2 (and related substances) scavenged by precipitation. MS thesis, Dept. of Geology, McMaster University, Hamilton, Ontario.

Krupa SV, Coscio MR, Jr, Wood FA. 1976. Evidence for multiple hydrogen-ion donor systems in rain. Water Air Soil Pollut. 6:415.

Lantzy RJ. Mackenzie FT. 1979. Atmospheric trace metals: Global cycles and assessment of man's impact. Geochim. Cosmochim. Acta 43:511.

Lazrus AL, Lorange E, Lodge JP, Jr. 1970. Lead and other metal ions in United States precipitation. Environ. Sci. Technol. 4:55.

Likens GE. 1972. The chemistry and precipitation in the central Finger Lakes region. Tech. Rep. 50, Water Resources and Marine Sciences Center, Cornell University, Ithaca, NY.

Liljestrand HM, Morgan JJ. 1978. Chemical composition of acid precipitation in Pasadena, CA. Environ. Sci. Technol. 12:1271.

Lockeretz W. 1974. Deposition of airborne mercury near point sources. Water Air Soil Pollut. 3:179.

Lundgren DA 1977. Remarks during Expert Meeting on Dry Deposition. Gothenburg, Sweden. (Available from WMO, Geneva.)

Martens CS, Harriss RC. 1973. Chemistry of aerosols, cloud droplets and rain in the Puerto Rican marine atmosphere. J. Geophys. Res. 78:949.

Matheson DH. 1979. Mercury in the atmosphere and in precipitation. In: Biogeochemistry of Mercury in the Environment, Nriagu JO, ed., Elsevier-North Holland, NY.

Matsunaga K. 1978. Mercury in sediments from the Okhotsk Sea and Funka Bay. Geochem. J. 12:287.

Matsunaga K, Goto T. 1976. Mercury in the air and precipitation. Geochem. J. 10:107.

McCall JG, Bush DS. 1978. Precipitation and throughfall chemistry in the San Francisco Bay area. J. Environ. Qual. 7:352.

McLean RAN. 1980. Methyl mercury transport in the environment: The role of atmospheric precipitation. Nature (in press).

McLean RAN, Findlay DM, Farkas MO. 1980. Mercury transport in the environment--sampling and analysis problems. In: Polluted Rain, Taribara TY, et al., eds., Plenum, NY.

Moore DI, Gosz JR, White CS. 1978. Impact of a ski basin on a mountain watershed. Water Air Soil Pollut. 10:81.

Murozumi M, Chow TJ, Patterson C. 1969. Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim. Cosmochim. Acta 33:1247.

National Academy of Sciences. 1978. An Assessment of Mercury in the Environment. Washington, D.C.

Norton SA, Dubiel RF, Sasseville DR, Davis RB. 1978. Paleolimnologic evidence for increased Zn loading in lakes of New England. Verh. Int. Ver. Theor. Angew Limnol. (Eng.) 20.

Norton SA, Hess CA, Davis RB. 1980. Rates of accumulation of heavy metals in pre- and post-European sediments in New England lakes. In: Atmospheric Input of Pollutants to Natural Waters, Eisenreich SJ, ed., Ann Arbor Science Pubs., Ann Arbor, MI (in press).

Nriagu JO. 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature 279:409.

Page AL, Ganje TO. 1979. Accumulations of lead in motor vehicle traffic density. Environ. Sci. Technol 4:140.

Pattenden NJ. 1974. Atmospheric concentration and deposition rates of some trace elements measured in the Swansea/Neath/ Port/ Talbot area. AERE Harwell Rep. R-7729, Her Majesty's Stationery Office, London.

_____. 1977. Remarks during Expert Meeting on Dry Deposition. Gothenburg, Sweden. (Available from WMO, Geneva).

Peirson DH, Cawse PA, Salmon L, Cambray RS. 1973. Trace elements in the atmospheric environment. Nature 241:252.

Peyton T, McIntosh A, Anderson V, Yost K. 1976. Aerial input of heavy metals into an aquatic ecosystem. Water Air Soil Pollut. 5:443-451.

Rahn KA. 1976. The chemical composition of the atmospheric aerosol. Technol. Rep., Graduate School of Oceanography, University of Rhode Island, Kingston.

Ronneau C, Cara J, Navarre JL, Priest P. 1978. An automatic sequential rain sample. Water Air Soil Pollut. 9:171.

Ruppert H. 1975. Geochemical investigations on atmospheric precipitation in a medium-sized city (Gottingen, FRG). Water Air Soil Pollut. 4:447.

Salmon L, Atkins DHF, Fisher EMR, Healy C, Law DV. 1977. Retrospective trend analysis of the content of United Kingdom air particulate material 1957-1974. AERE Harwell Rep. 8680, Her Majesty's Stationery Office, London.

Schlesinger WH, Reiners WA, Knopman DS. 1974. Heavy metal concentration and deposition in bulk precipitation in mountain ecosystems of New Hampshire, USA. Environ. Pollut. 6:39.

Schaefer VJ, Fuquay JJ. 1965. The detection of silver iodide in snow by neutron activation analysis. J. Rech. Atmos. 2:49.

Semb A. 1978. Deposition of trace elements from the atmosphere in Norway. Norwegian SNSF Project Res. Rep. FR-13178, Oslo.

Shiomi MT, Kuntz KW. 1973. Great Lakes precipitation chemistry: Part I, Lake Ontario basin. Sixteenth Great Lakes Res. Conference.

Siccama TG, Smith WH. 1978. Lead accumulation in a northern hardwood forest. Environ. Sci. Technol. 12:593.

Siegel SM, Siegel BZ. 1978. Mercury fallout in Hawaii. Water Air Soil Pollut. 9:113.

Slinn WGN, Katen PC, Wolf MA, et al. 1979. Wet and dry deposition and resuspension of AFCT/TFCT fuel processing radionuclides. Report Corvallis Air Resources Center, Oregon State University, SR-0980-10.

Söderlund R. 1975. Some preliminary views of atmospheric transport of matter to the Baltic Sea. Rep. AC-31 MISU-IMI, Arrhenius Laboratory, Stockholm.

Struempler AW. 1976. Trace metals in rain and snow during 1973 at Chadron, Nebraska. Atmos. Environ. 10:33.

Sugawara K, Okabe S, Tamaka M. 1961. Geochemistry of molybdenum in natural waters. (Eng.) Chem. Abstr. 57:590.

Tanner TM, Rancitelli LA, Haller WA. 1972. Multielement analysis of natural waters by neutron activation, assays, chemical separation, and gamma ray spectrometric techniques. Water Air Soil Pollut. 1:132.

Thornton JD, Eisenreich SJ, Munger JW, Gorham E. 1980. Trace metal and acid composition of rain and snow in northern Minnesota. In: Atmospheric Input of Pollutants to Natural Waters, Eisenreich SJ, ed., Ann Arbor Science Pubs., Ann Arbor, MI (in press).

Torrey S, ed. 1978. Trace contaminants from coal. Noyes Data Corporation, Park Ridge, NJ.

Turekian KK, Nozaki J, Benninger LK. 1977. Geochemistry of atmospheric radon and radon products, Volume 5 of Annu. Rev. Earth and Planet. Sci., Donath RA, ed., Annual Reviews, Inc., Palo Alto, CA.

U.S.DOE. 1979. U.S. Department of Energy. Environmental Measurements Laboratory Quarterly (EML-363).

U.S.EPA. 1976. U.S. Environmental Protection Agency. National Interim Primary Drinking Water Regulations. EPA 570/9-76-003.

Van Cleef J. 1908. Is there a type of storm path. Mon. Weather Rev. 36:56.

Vermeulen AJ. 1977. Immieeieonderzoek met behulp van regenvangers, opzet, ervaringen en resultaten. In: Dienst voor de Milieuhydiene, Prov. Waterstaat van Noord-Holland, Haarlem.

Volchok HL. 1977. Remarks during Expert Meeting on Dry Deposition. Gothenburg, Sweden. (Available from WMO, Geneva).

Volchok HL, Bogen J. 1973. Atmospheric trace metal studies. In: Chemical Analysis of the Environment, Ahuja S, ed., Plenum, New York.

Volchok HL, Graveson RT. 1976. Wet/dry fallout collection. Second Federal Conference on the Great Lakes, ICMSE Federal Council for Science and Technology, Great Lakes Commission.

Warburton JA, Young LG. 1972. Determination of silver in precipitation down to 10^{-11}m concentrations by ion exchange and neutron activation analysis. Anal. Chem. 44-2043.

Weiss H, Bertine K, Koide M, Goldberg EP. 1975. The chemical composition of a Greenland glacier. Geochim. Cosmochim. Acta 39:1.

Weiss H, Herron MM, Langway CC. 1978. Natural enrichment of elements in snow. Nature 274:352.

Whitby KT. 1973. On the multimodal nature of atmospheric aerosol size distributions. Paper presented at Seventh International Conference on Nucleation, Leningrad.

Whitby KT. Husar RB, Liu BYH. 1972. The aerosol size distribution of Los Angeles smog. J. Colloid Interface Sci. 39:177.

Wiener JG. 1979. Aerial inputs of Cd, Cu, Pb and Mn into a freshwater pond in the vicinity of a coal-fired power plant. Water Air Soil Pollut. 12:343.

Wisniewski J. 1975. Variability of rainwater silver concentration in south Florida. Florida Area Cumulus Experiment unpublished observations, Environmental Research Laboratories, NOAA, Boulder.

Wood JM. 1974. Biological cycles for toxic elements in the environment. Science 183:1049.

Zitko V, Carson WV. 1971. Heavy metals in the precipitation in the vicinity of St. Andrews, New Brunswick. Report Series 1129, Biological Station, Fisheries Res. Board, St. Andrews, Canada.

Zoller WH, Gladney ES, Duce RA. 1974. Atmospheric concentrations and sources of trace metals at the South Pole. Science 183:198.

Part I - APPENDIX A

Concentrations of Metals in the Atmosphere: Selected Data

The data presented here were classified into the following regions:

Remote -	Any areas of lowest concentration. There is a large discrepancy between data from the Antarctic and the Arctic (Norway, Greenland, Canada) with the latter having somewhat higher concentrations. Both sets of data have been included in the remote range until the discrepancy can be resolved.
Rural -	Any site not subject to the direct influence of local sources but representative of a regional background.
Urban -	Any site (in a city or elsewhere) subject to a local source.

When available, the first set of data for each element in each region is from Eisenreich et al. (1978). Reported concentrations for many elements varied widely, perhaps because of measuring errors. In addition, very few data have been reported for many toxic metals. For example, no remote data were available for Be or Sn, and only Dams and de Jonge (1976) reported remote values for Ag and Mo.

All citations are included in the Reference list at the end of Part I. Ranges of concentration are summarized in Table I-3; median concentrations are in Table I-4; ratios of the median concentrations in the rural and urban areas to the median remote concentration for each metal are in Table I-5.

Concentration of Metals in the Atmosphere
A Selection

	ng m^{-3}	Location	Reference
Ag			
Remote	0.01	Switzerland	Dams and de Jonge 1976
Rural	0.3	England	Salmon et al. 1977
Urban	1.1	Ohio	King et al. 1976
As			
Remote	0.17-1.47	USA, Europe	Eisenreich et al. 1978
	0.23	Switzerland	Dams and de Jonge 1976
Rural	0.31-2.5	Europe, Canada	Eisenreich et al. 1978
	4-10	England	Salmon et al. 1977
	12.1	Ohio	King et al. 1976
Urban	0.3-130	Canada, Europe, USA, N. Sea	Eisenreich et al. 1978
	17.4	Ohio	King et al. 1976
	17.5-26	Norway	Semb 1978
	5.0	Netherlands	Evendijk 1977
Be			
Rural	0.023	Ohio	King et al. 1976
Urban	0.14	Ohio	Ibid.
Cd			
Remote	0.0059-0.28	Europe, USSR, Indian Ocean (S)	Eisenreich et al. 1978
	0.5	Switzerland	Dams and de Jonge 1976
	0.003-0.62	N. Atlantic, S. Pole	Duce et al. 1975
Rural	0.124-1.96	Europe, Indian Ocean (N)	Eisenreich et al. 1978
	1.55	Ohio	King et al. 1976
	0.07-0.33	Norway	Semb 1978
Urban	0.07-118	Europe, USSR, USA, Japan, Bermuda, N. Atlantic	Eisenreich et al. 1978
	3.9	Ohio	King et al. 1976
	2.8	Netherlands	Evendijk 1977

Metal Concentrations: Atmosphere (continued)

	ng m^{-3}	Location	Reference
Co			
Remote	0.013-0.26	Europe, S. Pole, Gulf of Guinea	Eisenreich et al. 1978
	0.00084	S. Pole	Zoller et al. 1974
	0.045	Switzerland	Dams and de Jonge 1976
	0.006-0.09	N. Atlantic, S. Pole	Duce et al. 1975
	0.042-0.061	Norway	Semb 1978
	0.6-3	Greenland, Easter Islands	Feely et al. 1979
Rural	0.04-0.245	Europe, Canada, Ivory Coast, Atlantic Coast,	Eisenreich et al. 1978
	0.2-2.0	England	Salmon et al. 1977
	0.75	Ohio	King et al. 1976
	0.42-0.214	Norway	Semb 1978
Urban	0.07-43	Europe, USA, Japan, Hawaii, Ivory Coast, N. Sea, N. Atlantic, Sudan	Eisenreich et al. 1978
	2.6	Ohio	King et al. 1976
	3.5	Netherlands	Evendijk 1977
	36	IML sampling sites in the Americas (50°N-53°S)	Feely et al. 1979
Cr			
Remote	0.11-1.29	Europe, Canada, S. Pole, Gulf of Guinea	Eisenreich et al. 1978
	0.0053	S. Pole	Zoller et al. 1974
	0.36	Switzerland	Dams and de Jonge 1976
	0.07-1.1	N. Atlantic, S. Pole	Duce et al. 1975
	0.22-0.35	Norway	Semb 1978
	<1-2	Greenland, Easter Islands	Feely et al. 1979
Rural	0.618-65	Canada, Ivory Coast, Europe, USSR, Atlantic Ocean	Eisenreich et al. 1978
	5-10	England	Salmon et al. 1977
	3.4	Ohio	King et al. 1976
	0.22-1.30	Norway	Semb 1978

Metal Concentrations: Atmosphere (continued)

	ng m^{-3}	Location	Reference
Cr (continued)			
Urban	0.39-1100	USA, Europe, Japan, Bute, Hawaii, Bermuda, N. Sea, N. Atlantic, Atlantic Ocean, Sudan	Eisenreich et al. 1978
	19	Ohio	King et al. 1976
	16	Netherlands	Evendijk 1977
Cu			
Remote	0.04-2.1	Europe, Hawaii, USSR, Indian Ocean (S), S. Pole	Eisenreich et al. 1978
	0.029-0.036	S. Pole	Zoller et al. 1974
	0.024	Switzerland	Dams and de Jonge 1976
	0.12-10	N. Atlantic, S. Pole	Duce et al. 1975
	1.6-2.4	Norway	Semb 1978
	<0.6-2	Greenland, Easter Islands	Feely et al. 1979
Rural	0.9-12	Europe, Canada, USSR, Indian Ocean (N)	Eisenreich et al. 1978
	72	Ohio	King et al. 1976
	2.2-13.9	Norway	Semb 1978
Urban	0.12-4000	USA, Europe, USSR, Japan, Canada, Bermuda, N. Atlantic, Atlantic Ocean, Tasmania, Sudan	Eisenreich et al. 1978
	130	Ohio	King et al. 1976
	255	Netherlands	Evendijk 1977
	343	IML sampling sites in the Americas (50°N-53°S)	Feely et al. 1979
Hg			
Remote	0.208	Gulf of Guinea	Eisenreich et al. 1978
	0.03	Switzerland	Dams and de Jonge 1976
Rural	0.02-0.428	Europe, Ivory Coast	Eisenreich et al. 1978
	0.5-4	England	Salmon et al. 1977
	0.223	Ohio	King et al. 1976
Urban	0.06-11.2	USA, Europe, Ivory Coast, N. Atlantic Sudan	Eisenreich et al. 1978

Metal Concentrations: Atmosphere (continued)

	ng m^{-3}	Location	Reference
Mn			
Remote	0.2-4.5	Europe, Canada, USSR, Indian Ocean (S), S. Pole, Atlantic Ocean	Eisenreich et al. 1978
	0.0103	S. Pole	Zoller et al. 1974
	1.5	Switzerland	Dams and de Jonge 1976
	0.05-54	N. Atlantic, S. Pole	Duce et al. 1975
	1.4-3.5	Norway	Semb 1978
	<1-3	Greenland, Easter Islands	Feely et al. 1979
Rural	1.1-647	Canada, Europe, Ivory Coast, USSR, Indian Ocean (N), Atlantic Ocean	Eisenreich et al. 1978
	15-60	England	Salmon et al. 1977
	66.3	Ohio	King et al. 1976
	1.4-20.7	Norway	Semb 1978
Urban	1.7-5400	USA, Europe, USSR, Bute, Hawaii, Bermuda, N. Sea, Atlantic Ocean, Sudan	Eisenreich et al. 1978
	148	Ohio	King et al. 1976
	80	Netherlands	Evendijk 1977
	269	IML sampling sites in the Americas (50°N-53°S)	Feely et al. 1979
Mo			
Remote	0.3	Switzerland	Dams and de Jonge 1976
Urban	<1	Ohio	King et al. 1976
	3.4	Netherlands	Evendijk 1977
Ni			
Remote	0.35-0.38	Europe, USSR, Indian Ocean (S), S. Pole	Eisenreich et al. 1978
	0.6-3	Greenland, Easter Islands	Feely et al. 1979
Rural	1.3-4.3	Europe, USSR, Indian Ocean (N)	Eisenreich et al. 1978
	10-50	England	Salmon et al. 1977

Metal Concentrations: Atmosphere (continued)

	ng m^{-3}	Location	Reference
Ni (continued)			
Urban	0.2-1000	Europe, USSR, USA, Japan, Bute, Hawaii, N. Sea,	Eisenreich et al. 1978
	0.3	Netherlands	Evendijk 1977
	35	IML sampling sites (50°N-53°S)	Feely et al. 1979
Pb			
Remote	0.23-38	Europe, Canada, Hawaii, USSR, Indian Ocean (S), S. Pole, Atlantic Ocean	Eisenreich et al. 1978
	0.20	S. Pole	Zoller et al. 1974
	4.4	Switzerland	Dams and de Jonge 1976
	0.10-64	N. Atlantic, S. Pole	Duce et al. 1975
	0.6-10	Greenland, Easter Islands	Feely et al. 1979
Rural	0.6-64	Europe, USSR, Indian Ocean (N), Atlantic Ocean	Eisenreich et al. 1978
	100-200	England	Salmon et al. 1977
	451	Ohio	King et al. 1976
	9.4-23.6	Norway	Semb 1978
Urban	0.8-8300	USA, Europe, USSR, Japan, Bute, Hawaii, Bermuda, N. Sea, Sudan Tasmania, Atlantic Ocean	Eisenreich et al. 1978
	759	Ohio	King et al. 1976
	4150	IML sampling sites in the Americas (50°N-53°S)	Feely et al. 1979
Sb			
Remote	0.2	Switzerland	Dams and de Jonge 1976
	0.05-0.64	N. Atlantic, S. Pole	Duce et al. 1975
	0.18-0.35	Norway	Semb 1978

Metal Concentrations: Atmosphere (continued)

	ng m^{-3}	Location	Reference
Sb (continued)			
Rural	1.5-7	England	Salmon et al. 1977
	6.29	Ohio	King et al. 1976
	0.18-1.01	Norway	Semb 1978
Urban	43	Ohio	King et al. 1976
	12	Netherlands	Evendijk 1977
Se			
Remote	0.042	Switzerland	Dams and de Jonge 1976
	0.09-0.40	N. Atlantic S. Pole	Duce et al. 1975
	0.09-0.17	Norway	Semb 1978
Rural	1.2-2.2	England	Salmon et al. 1977
	3.3	Ohio	King et al. 1976
	0.09-0.66	Norway	Semb 1978
Urban	4.7	Ohio	King et al. 1976
Sn			
Rural	55	Ohio	King et al. 1976
Urban	99	Ohio	Ibid.
V			
Remote	0.0015-2.15	Europe, Canada, Hawaii, S. Pole	Eisenreich et al. 1978
	0.0015	S. Pole	Zoller et al. 1974
	0.29	Switzerland	Dams and de Jonge 1976
	0.06-14	N. Atlantic, S. Pole	Duce et al. 1975
	<1-3	Greenland, Easter Islands	Feely et al. 1979
Rural	0.37-5.33	Canada, Europe	Eisenreich et al. 1978
	5-15	England	Salmon et al. 1977
	5.96	Ohio	King et al. 1976
Urban	2.8-600	USA, Europe, Japan, Bute, Hawaii, N. Sea	Eisenreich et al. 1978
	10.5	Ohio	King et al. 1976
	39	Netherlands	Evendijk 1977
	185	IML sampling sites in the Americas (50°N-53°S)	Feely et al. 1979

Metal Concentrations: Atmosphere (continued)

	ng m^{-3}	Location	Reference
Zn			
Remote	0.03-31	Europe, S. Pole	Eisenreich et al. 1978
	0.030	S. Pole	Zoller et al. 1974
	9.9	Switzerland	Dams and de Jonge 1976
	0.3-27	N. Atlantic	Duce et al. 1975
	4.7-7.8	Norway	Semb 1978
	<0.8-3	Greenland, Easter Islands	Feely et al. 1979
Rural	3.8-90.7	Europe, Canada	Eisenreich et al. 1978
	100-1200	England	Salmon et al. 1977
	264	Ohio	King et al. 1976
	5.8-45	Norway	Semb 1978
Urban	0.3-3120	USA, Europe, Japan, Bute, Hawaii, Canada, Bermuda, N. Sea, N. Atlantic, Atlantic Ocean, Tasmania, Sudan	Eisenreich et al. 1978
	413	Ohio	King et al. 1976
	350	Netherlands	Evendijk 1977
	2800	IML sampling sites in the Americas (50°N-53°S)	Feely et al. 1979

Part I - APPENDIX B

Concentrations of Metals in Wet Deposition

Because of the lack of systematically collected data for other metals, the results of many different investigations of the metal concentrations in wet deposition have been divided into categories for remote, rural, and urban areas. This compilation shows how few data are available for most metals and how few toxic metals have ever been studied. No studies have measured Be, Sn, Te, and Tl and less than fifteen studies have measured Ag, As, Co, Cr, Sb, Se, and V. All citations are included in the reference list at the end of Part I.

The ranges of metal concentrations in precipitation vary widely within these three categories--up to four orders of magnitude for some metals--reflecting the different methods of sampling and analyses and the many different locations. For example:

(1) Observation periods range from as short as one month to as long as two years;
(2) Collection frequencies range from event sampling to monthly and to even yearly sampling;
(3) Collector designs are different;
(4) Samples are treated differently (e.g., filtered vs. unfiltered);
(5) Analytical methods vary considerably;
(6) Distinctions between remote, rural, and urban sites are subjective, particularly between rural and urban sites.

Because of these differences in sampling techniques, the lack of data, and the wide variations in concentrations, it is difficult to assign a representative concentration value for any given metal in any given area.

Ranges of metal concentrations are summarized in Table I-6; the median concentrations are in Table I-7; the ratios of median metal concentrations in the urban and rural areas to those in the remote areas are in Table I-8.

Concentrations of Metals in Wet Deposition

	Precipitation			
	Type	μg ℓ^{-1}	Location	Reference
Ag				
Remote	Snow	0.006	Antarctica	Boutron & Lorius 1979
		0.010	Greenland	Boutron 1979c
		0.008		Ibid.
Rural	Rain	0.48	South Florida	Wisniewski 1975
		0.01	Washington	Tanner et al. 1972
	Rain/snow	0.084	Nebraska	Struempler 1976
	Snow	0.023	Lake Erie	Warburton & Young 1972
		0.073	South Illinois	Gatz 1975
		0.040	Colorado	Schaefer & Fuquay 1965
		0.036	Montana	Warburton & Young 1972
Urban	Rain	3.2	Heidelberg	Bogen 1974
As				
Remote	Ice/snow	0.019	Greenland	Weiss et al. 1975
Rural	Bulk	3.0	Lake Erie	Konasewich et al. 1978
		1.0	Lake Huron	Ibid.
		1.6	Uraymines (UK)	Peirson et al. 1973
		9.6	Swansea (UK)	Pattenden 1974
		3.9	Great Britain	Cawse 1974
		0.5	Washington	Dethier 1977
	Rain	<0.1	Washington	Tanner et al. 1972
		0.5	N. Norway	Hanssen et al. 1980
Urban	Bulk	7.0	Seattle	Larson 1977
Cd				
Remote	Rain	<0.1	NWT (Canada)	Kramer 1973
	Snow	1.4	Antarctica	Gjessing & Gjessing 1973
		0.004		Boutron & Lorius 1979
		0.007		Boutron 1979a
		0.005	Greenland	Boutron 1979b
		0.011		Ibid.
	Ice/snow	0.008	Greenland	Herron et al. 1977
		0.639		Weiss et al. 1975
Rural	Bulk	0.5	South Carolina	Wiener 1979
		0.22	N. Norway	Hanssen et al. 1980
		1.0	Lake Ontario	Shiomi & Kuntz 1973
		2.0	Lake Erie	Konasewich et al. 1978
		2.0	Lake Huron	Ibid.
		0.6	Lake Michigan-S	Eisenreich 1980

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	μg ℓ$^{-1}$	Location	Reference
Cd (continued)				
		0.4	Lake Michigan-N	Ibid.
		<17.7	Uraymines (UK)	Peirson et al. 1973
		18	Great Britain	Cawse 1974
		0.6	New Hampshire	Schlesinger et al. 1974
		0.18-0.30	NE. Minnesota	Eisenreich et al. 1978
	Rain	46.0	Lake Erie	Konasewich et al. 1978
		1.0	Lake Superior	Eisenreich et al. 1978
		10.5	Tennessee	Andren et al. 1975
		4.0	Belgium	Ronneau et al. 1978
		7.0	Sweden	Dickson 1975
		0.3		Söderland 1975
		0.27	Norway	Semb 1978
		0.20	Denmark	Hovmand 1976
		0.6	North Holland	Vermeulen 1977
		<2.0	Twin Cities	Krupa et al. 1976
		0.4-80	Delaware	Biggs et al. 1973
		0.6	New Brunswick	Zitko & Carson 1971
	Rain/snow	0.31	Nebraska	Struempler 1976
		0.15	NE. Minnesota	Thornton et al. 1980
		0.18	N. Minnesota	Ibid.
		0.73	SW.North Dakota	Ibid.
	Snow	3.4	Norway	Johannessen & Henriksen 1978
		2.5		Henriksen 1972
		0.08	Alaska	Weiss et al. 1978
Urban	Bulk	19.0	London	Harrison et al. 1975
	Rain	0.5	Gottingen (FRG)	Ruppert 1975
	Rain/snow	2.3	Minneapolis	Thornton et al. 1980
	Snow	0.7	Ottawa	Jonasson 1973
Co				
Rural	Bulk	7.0	Lake Erie	Konasewich et al. 1978
		2.0	Lake Huron	Ibid.
		<1.0	Lake Michigan-S	Eisenreich 1980
			Lake Michigan-N	Ibid.
		0.25	Uraymines (UK)	Peirson et al. 1973
		3.6	Swansea (UK)	Pattenden 1974
			United Kingdom	Cawse 1974
		<1.4	NE. Minnesota	Eisenreich et al. 1978
	Rain	1.5	Lake Superior	Ibid.
		0.01	Washington	Tanner et al. 1972
Urban	Rain	1.8	Heidelberg	Bogen 1974

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	$\mu g\ \ell^{-1}$	Location	Reference
Cr				
Rural	Bulk	2.9	Uraymines (UK)	Peirson et al. 1973
		8.3	Swansea (UK)	Pattenden 1974
		6.6	United Kingdom	Cawse 1974
	Rain	1.9	Tennessee	Andren & Lindberg 1977
		30.0	Belgium	Ronneau et al. 1978
		<5.0	Sweden	Dickson 1975
		0.2		Söderland 1975
		<0.1	Washington	Tanner et al. 1972
	Rain/snow	0.24	NE. Minnesota	Thornton et al. 1980
		0.27	N. Minnesota	Ibid.
		0.44	SW.North Dakota	Ibid.
Urban	Rain	15.0	New York City	Volchok & Bogen 1973
		3.6	Heidelberg	Bogen 1974
	Rain/snow	0.51	Minneapolis	Thornton et al. 1980
Cu				
Remote	Rain	<0.5	NWT (Canada)	Kramer 1973
	Snow	16	Antarctica	Gjessing & Gjessing 1973
		0.047		Boutron & Lorius 1979
		0.035		Boutron 1979a,b
		0.074	Greenland	Boutron 1979b,c
		0.055		Ibid.
	Ice/snow	0.851		Weiss et al. 1975
Rural	Bulk	6.0	Lake Ontario	Shiomi & Kuntz 1973
		9.0	Lake Erie	Konasewich et al. 1978
		7.0	Lake Huron	Ibid.
		6.0	Lake Michigan-S	Eisenreich 1980
		3.0	Lake Michigan-N	Ibid.
		23.0	Uraymines (UK)	Peirson et al. 1973
		57.0	Swansea (UK)	Pattenden 1974
		26.0	England	Cawse 1974
		21.0	United States	Lazrus et al. 1970
		5.8-7.9	NE. Minnesota	Eisenreich et al. 1978
		2.8	Washington	Dethier 1977
		2.3	South Carolina	Wiener 1979
	Rain	13.0	Lake Erie	Konasewich et al. 1978
		23.0	Lake Superior	Eisenreich et al. 1978
		14.4	Tennessee	Andren & Lindberg 1977
		30.0	Belgium	Ronneau et al. 1978
		9.0	Sweden	Dickson 1975
		7.0		Söderland 1975

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	$\mu g\ \ell^{-1}$	Location	Reference
Cu (continued)				
		5.3	Norway	Semb 1978
		1.4	Denmark	Hovmand 1976
		6.6	N. Holland	Vermeulen 1977
		<10.0	Twin Cities	Krupa et al. 1976
		2.0	Central Texas	Cooper & Lopez 1976
		0.3-60	Delaware	Biggs et al. 1973
		150	Pennsylvania	Chan et al. 1976
		6.4	New Brunswick	Zitko & Carson 1971
		0.4	Washington	Tanner et al. 1972
		0.8	Menlo Park, CA	Kennedy et al. 1979
	Rain/snow	4.4	Nebraska	Struempler 1976
		2.1	NE. Minnesota	Thornton et al. 1980
			N. Minnesota	Ibid.
		3.9	SW.North Dakota	Ibid.
	Snow	<1.0	Manitoba	Beamish & Van Loon 1977
		3.0	Ontario	Jonasson 1973
		13.0	Norway	Johannessen & Henriksen 1978
		33.0		Henriksen 1972
		9.5	New Mexico	Moore et al. 1978
Urban	Bulk	6.4	San Francisco	McCall & Bush 1978
		20.0	Seattle	Larson 1977. (Personal communication to S. A. Norton.)
	Rain	67.0	New York City	Volchok & Bogen 1973
		6.8	Gottingen (FRG)	Ruppert 1975
		120	Pittsburgh	Chan et al. 1976
	Rain/snow	8.2	Minneapolis	Thornton et al. 1980
	Snow	30	Ottawa	Jonasson 1973
Hg				
Remote	Ice	0.429	Greenland	Herron et al. 1976
		0.111		Carr & Wilkniss 1973
	Ice/snow	0.011	Greenland	Appelquist et al. 1978
		0.048		Weiss et al. 1975
Rural	Bulk	<0.2	Uraymines (UK)	Peirson et al. 1973
		0.4	England	Cawse 1974
		0.06	New Hampshire	Schlesinger et al. 1974
	Rain	0.18	Tennessee	Andren & Lindberg 1977
		0.2	Sweden	Söderland 1975
		<1.0-3.6	Central Texas	Cooper & Lopez 1976
		0.11	New Brunswick	Zitko & Carson 1971
		<0.1	Washington	Tanner et al. 1972

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	$\mu g\ \ell^{-1}$	Location	Reference
Hg (continued)				
	Snow	<0.01	East Ontario	Jonasson 1973
		<0.005	Alaska	Weiss et al. 1978
		0.05-0.10	NW. Quebec	McLean et al. 1980
		0.08	Quebec	Matheson 1979
Urban	Rain	0.04	Gottingen (FRG)	Ruppert 1975
		1.3	Heidelberg	Bogen 1974
		3.5-4.0	Canada	NAS 1978
		0.002	Japan	Matsunaga & Goto 1976
	Snow	0.069	Ottawa	Jonasson 1973
		0.05-2.0	Quebec	Matheson 1979
Mn				
Remote	Rain	2	South Pacific	Volchok 1979. (Personal communication to S. Eisenreich.)
	Snow	0.018	Antarctica	Boutron & Lorius 1979
		0.32	Greenland	Boutron 1979c
	Ice	0.215		Herron et al. 1977
	Ice/snow	0.139		Ibid.
		0.250		Weiss et al. 1975
Rural	Bulk	2.2	South Carolina	Wiener 1979
		4	N. Norway	Hanssen et al. 1980
		37	Lake Michigan-S	Eisenreich 1980
		15	Lake Michigan-N	Ibid.
		8.1	Uraymines (UK)	Peirson et al. 1973
		49	Swansea (UK)	Pattenden 1974
		20	England	Cawse 1974
		11	USSR-E	Drozdova & Makhonko 1970
	Rain	12	Lake Superior	Eisenreich et al. 1978
		14.8	Tennessee	Andren & Lindberg 1977
		5	Central New York	Likens 1972
		35	New Jersey	Volchok 1979. (Personal communication to S. Eisenreich.)
		0.1-6.0	Menlo Park	Kennedy et al. 1979
		10	Oregon	Volchok 1979. (Personal communication to S. Eisenreich.)
		84	Belgium	Ronneau et al. 1978
		5	Sweden	Dickson 1975
		11		Söderland 1975
		11	Norway	Semb 1978
		0.19	Washington	Tanner et al. 1972

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	µg ℓ$^{-1}$	Location	Reference
Mn (continued)				
	Rain/snow	5.2	Nebraska	Struempler 1976
		3.2	NE. Minnesota	Thornton et al. 1980
		5.6	N. Minnesota	Ibid.
		22	SW.North Dakota	Ibid.
	Snow	<1	Manitoba	Beamish & Van Loon 1977
		17	Norway	Johannessen & Henriksen 1978
		22	S. Norway	Elgmork et al. 1973
		<15	E. Ontario	Jonasson 1973
		0.9	Alaska	Weiss et al. 1978
Urban	Bulk	2.7	San Francisco	McCall & Bush 1978
	Rain	16	New York City	Volchok & Bogen 1973
		25	Gottingen (FRG)	Ruppert 1975
		22	Pittsburgh	Chan et al. 1976
		25	Heidelberg	Bogen 1974
		1.9	Los Angeles	Liljestrand & Morgan 1978
		80	New York City	Volchok 1979
	Rain/ Snow	26	Minneapolis	Thornton et al. 1980
Mo				
Urban	Snow	0.2	Nagoya, Japan	Sugawara et al. 1961
Ni				
Remote	Rain	<0.1	NWT (Canada)	Kramer 1973
Rural	Bulk	4.0	Lake Ontario	Shiomi & Kuntz 1973
		27	Lake Erie	Konasewich et al. 1978
		2	Lake Huron	Ibid.
		0.9-1.7	NE. Minnesota	Thornton et al. 1980
		4.0	United States	Lazrus et al. 1970
		6	Uraymines (UK)	Peirson et al. 1973
		35	Swansea (UK)	Pattenden 1974
		12	England	Cawse 1974
		3.8	USSR-E	Drozdova & Makhonko 1970
	Rain	<3	Lake Superior	Eisenreich et al. 1978
		5.7	Tennessee	Andren & Lindberg, 1977
		48	Sweden	Dickson 1975
		5		Söderland 1975
		0.6	Denmark	Hovmand 1976

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	$\mu g\ \ell^{-1}$	Location	Reference
Ni (continued				
	Rain/snow	1.5	NE. Minnesota	Thornton et al. 1980
		1.5	N. Minnesota	Ibid.
		3.6	SW.North Dakota	Ibid.
	Snow	<2.0	Manitoba	Beamish and Van Loon 1977
		8.2	New Mexico	Moore et al. 1978
Urban	Rain	114	New York City	Volchok & Bogen 1973
	Rain/snow	2.4	Minneapolis	Thornton et al. 1980
	Snow	17	Ottawa	Jonasson 1973
Pb				
Remote	Rain	<1.0	NWT (Canada)	Kramer 1973
	Snow	1.6	Antarctica	Gjessing & Gjessing 1973
		0.040		Boutron & Lorius 1979
		0.033		Boutron 1979b
		0.02		Murozumi et al. 1969
		0.41	Greenland	Ibid.
		0.229		Ibid.
		0.2		Ibid.
	Ice/snow	0.14		Herron et al. 1977
Rural	Bulk	20	Lake Ontario	Shiomi & Kuntz 1973
		11	Lake Erie	Konasewich et al. 1978
		12	Lake Huron	Ibid.
		39	Lake Michigan-S	Eisenreich 1980
		13	Lake Michigan-N	Ibid.
		13.4	New Hampshire	Schlesinger et al. 1974
		7.1-7.8	NE. Minnesota	Eisenreich et al. 1978
		3.2	Washington	Dethier 1977
		34	United States	Lazrus et al. 1970
		39	Uraymines (UK)	Peirson et al. 1973
		97	Swansea (UK)	Pattenden 1974
		40	England	Cawse 1974
		3.5	N. Norway	Hanssen et al. 1980
		4.7	USSR-E	Drozdova & Makhonko 1970
		6.6	South Carolina	Wiener 1979
	Rain	17	Lake Erie	Konasewich et al. 1978
		15.6	Tennessee	Andren & Lindberg 1977
		<20	Twin Cities	Krupa et al. 1976
		4	Central Texas	Cooper & Lopez 1976
		3-35	Menlo Park	Kennedy et al. 1979
		0.6-60	Delaware	Biggs et al. 1973
		19	Pennsylvania	Chan et al. 1976
		2.8	New Brunswick	Zitko & Carson 1971
		51	Belgium	Ronneau et al. 1978

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	μg ℓ$^{-1}$	Location	Reference
Pb (continued)				
		64	Sweden	Dickson 1975
		10		Söderland 1975
		13	Norway	Semb 1978
		7.0	Denmark	Hovmand 1976
		28	N. Holland	Vermeulen 1977
	Rain/snow	4.8	Nebraska	Struempler 1976
		7.1	NE. Minnesota	Thornton et al. 1980
		5.7	N. Minnesota	Ibid.
		8.0	SW.North Dakota	Ibid.
	Snow	<1.0	Manitoba	Beamish & Van Loon 1977
		7.5	E. Ontario	Jonasson 1973
		15.1	New Mexico	Moore et al. 1978
		30	Norway	Johannessen & Henriksen 1978
		15		Henriksen 1972
		30	S. Norway	Elgmork et al. 1973
Urban	Bulk	190	London	Harrison et al. 1975
		20	Seattle	Larson 1977
	Rain	147	New York City	Volchok & Bogen 1973
		5.4	Gottingen (FRG)	Ruppert 1975
		41	Pittsburgh	Chan et al. 1976
		75	Los Angeles	Liljestrand & Morgan 1978
	Rain/ snow	31	Minneapolis	Thornton et al. 1980
	Snow	76	Ottawa	Jonasson 1973
Sb				
Remote	Ice/snow	0.034	Greenland	Weiss et al. 1975
Se				
Rural	Bulk	0.34	Uraymines (UK)	Peirson et al. 1973
		1.1	Swansea (UK)	Pattenden 1974
		0.59	England	Cawse 1974
		1	N. Norway	Hanssen et al. 1980
V				
Remote	Ice	0.022	Greenland	Herron et al. 1976
	Ice/snow	0.016		Herron et al. 1977
		0.31	N. Norway	Hanssen et al. 1980
Rural	Bulk	4.1	Uraymines (UK)	Peirson et al. 1973
		13	Swansea (UK)	Pattenden 1974
		8.9	England	Cawse 1974

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	$\mu g\ \ell^{-1}$	Location	Reference
V (continued)				
	Rain	4.7	N. Holland	Vermeulen 1977
		<20	Twin Cities	Krupa et al. 1976
		1.1	Puerto Rico	Martens & Harriss 1973
	Snow	0.13	Alaska	Weiss et al. 1978
Urban	Rain	68	New York City	Volchok & Bogen 1973
Zn				
Remote	Rain	<1.0	NWT (Canada)	Kramer 1973
	Snow	27	Antarctica	Gjessing & Gjessing 1973
		0.001		Boutron & Lorius 1979
		0.031		Boutron 1979a,b
		0.78	Greenland	Boutron 1979b,c
		0.293		Ibid.
	Ice	0.215	Greenland	Herron et al. 1976
	Ice/snow	0.224		Herron et al. 1977
		1.1		Weiss et al. 1975
Rural	Bulk	80	Lake Ontario	Shiomi & Kuntz 1973
		140	Lake Erie	Konasewich et al. 1978
		53	Lake Huron	Ibid.
		57	Lake Michigan-S	Eisenreich 1980
		33	Lake Michigan-N	Ibid.
		0.5	Washington	Dethier 1977
		110	United States	Lazrus et al. 1970
		85	Uraymines (UK)	Peirson et al. 1973
		160	Swansea (UK)	Pattenden 1974
		120	England	Cawse 1974
		7.8	N. Norway	Hanssen et al. 1980
	Rain	130	Lake Erie	Konasewich et al. 1978
		176	Lake Superior	Eisenreich et al. 1978
		34.9	Tennessee	Andren & Lindberg 1977
		15	Twin Cities	Krupa et al. 1976
		2-13	Menlo Park	Kennedy et al. 1979
		3	Central Texas	Cooper & Lopez 1976
		82	Pennsylvania	Chan et al. 1976
		3	Washington	Tanner et al. 1972
		251	Belgium	Ronneau et al. 1978
		311	Sweden	Dickson 1975
		60		Söderland 1975
		29	Norway	Semb 1978
		15	Denmark	Hovmand 1976
		187	N. Holland	Vermeulen 1977
		36	New Brunswick	Zitko & Carson 1971

Metal Concentrations: Wet Deposition (continued)

	Precipitation			
	Type	$\mu g\ \ell^{-1}$	Location	Reference
Zn (continued				
	Rain/ snow	10	Nebraska	Struempler 1976
		93	NE. Minnesota	Thornton et al. 1980
		99	N. Minnesota	Ibid.
		147	SW.North Dakota	Ibid.
	Snow	<1.0	Manitoba	Beamish & Van Loon 1977
		10	E. Ontario	Jonasson 1973
		1.7	Alaska	Weiss et al. 1978
		63	Norway	Johannessen & Henriksen 1978
		56		Henriksen 1972
		45	S. Norway	Elgmork et al. 1973
Urban	Bulk	16	San Francisco	McCall & Bush 1978
		6	Seattle	Larson 1977
	Rain	280	New York City	Volchok & Bogen 1973
		88	Pittsburgh	Chan et al. 1976
		48	Gottingen (FRG)	Ruppert 1975
	Rain/ snow	40	Minneapolis	Thornton et al. 1980
	Snow	20	Bergen, Norway	Forland & Gjessing 1975
		22	Ottawa	Jonasson 1973

Part II - TRACE ORGANICS: A REVIEW AND ASSESSMENT

S. J. Eisenreich (Chairman), T. F. Bidleman, T. J. Murphy,
A. R. Davis, D. A. Banning, C. S. Giam,
F. J. Priznar and M. D. Mullin

1. INTRODUCTION

In recent years, there has been a growing concern that atmospheric transport and deposition are responsible for the accumulation of trace organic constituents, such as DDT, PCBs, and others, in areas of the world where local sources are absent (Nisbet and Sarofim 1972; Risebrough et al. 1968a, b; Peel 1975). Although atmospheric concentrations often range from $<10^{-9}$ to 10^{-8} g m^{-3} and thus are very low, atmospheric input into aquatic ecosystems contributes to and in some cases is responsible for the accumulation of trace organics in every level of the food chain. In some instances, a complete fishery may be eliminated (as in Lake Michigan where PCB concentrations in fish from 2 to 19 mg kg^{-1} far exceed the FDA guidelines of 2 mg kg^{-1} for edible fish).

Anthropogenic chlorinated (CH) and nonchlorinated hydrocarbons are hydrophobic compounds of low water solubility that partition rapidly into lipid layers of plankton and fish and concentrate in the food chain. While food chain bioconcentration at lower trophic levels may not be a controlling factor in the high concentrations observed in plankton (Clayton et al. 1972), it is probably the source for the concentrations of these materials found in fish. The bioconcentration of some CHs may be controlled by equilibrium partitioning between the internal lipid pools of the biota and ambient water. Once CHs are incorporated, they may alter species composition of mixed phytoplankton assemblages (Mosser et al. 1972), inhibit zooplankton reproduction (Wildish 1972), and decrease phytoplankton biomass and natural species size, thereby altering and contaminating harvestable fish. Trace concentrations of some CHs in the 10^{-9} g ℓ^{-1} range, derived mainly from atmospheric deposition, can support potentially toxic concentrations in numerous compartments of the aquatic ecosystem.

The atmospheric processes responsible for the removal of trace organics from the atmosphere are wet deposition, dry particle deposition, and dry-vapor deposition (Figure II-1). A knowledge of gas-particle-phase distributions of trace organics in the atmosphere is critical to understanding the deposition processes. Gases may be scavenged from the atmosphere by precipitation; the extent of scavenging, or solubility coefficient (α),

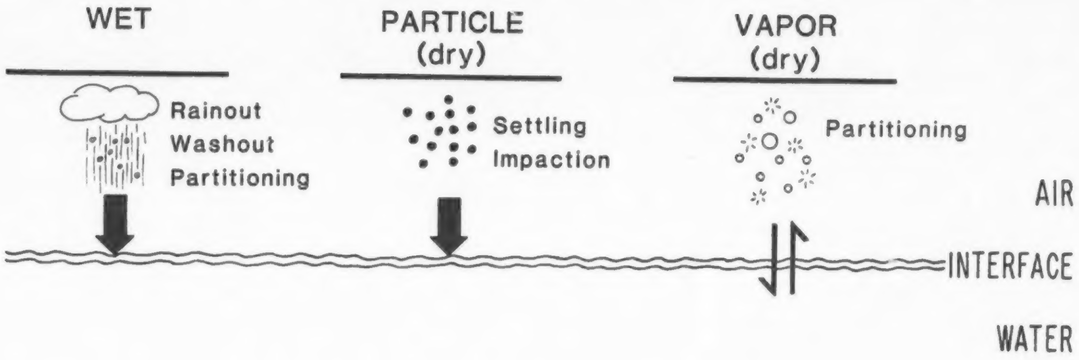


Figure II-1. Atmospheric input of anthropogenic organics to natural waters.

is dependent upon the magnitude of Henry's law constant H, which is the reciprocal of α. Particle removal from the atmosphere by wet deposition can also be estimated from the washout coefficient, W (see Part III). In both cases, the concentration of the trace organic in the atmosphere at a reference height must be known.

Dry particle deposition can be estimated from the deposition velocity and the particulate trace-organic concentration at a reference height. The deposition velocities of trace organics to different receptor surfaces are not well known. The flux of vapor-phase trace organics into aqueous systems depends on the overall mass-transfer rates across the air/water interface and on the "dissolved" concentration of the trace organic in water in equilibrium with the concentration in the atmosphere. Here again, Henry's law constant H becomes important. Therefore, several parameterizations are required to estimate the wet and dry flux of trace organics to water.

Trace organics entering a water body from the atmosphere first come into contact with the surface film and must be transported through the film. They are then subjected to the biological uptake, aerosolization/volatilization, and selective chemical or biological degradation that determine the mass and species available to the water column. Hydrophobic organics, such as DDT, PCBs, and PAHs, exhibit low water solubilities and largely associate with biotic and abiotic particulates. However, even in unusual cases when the particle:water distribution coefficient is high (10^4-10^5), a large fraction of the trace-organic concentration may be dissolved because of low concentrations of suspended particles (i.e., low adsorptive surface area). Ultimately, trace organics that are biologically transformed or adsorbed to particulates accumulate in lake sediments and lipid compartments of the water column. The chemical and physical properties of trace organics are important because deposition and emission processes are, to some extent, influenced by aqueous cycling.

This section discusses the processes important in atmospheric trace-organic fluxes to water, identifies the physical properties and parameterizations necessary to estimate fluxes, summarizes what is known about trace organics in the atmosphere, and applies flux calculations to a specific system.

2. VAPOR AND PARTICLE DISTRIBUTION OF ATMOSPHERIC ORGANICS

High-molecular-weight organics in the atmosphere are present in the vapor phase and are adsorbed on particulate matter. Vapor-aerosol partitioning in the atmosphere depends on the vapor pressure of the organic compound, the size and surface area of the suspended particulates, and the organic content of the aerosol (Junge 1977). Vapor-aerosol distributions calculated from vapor pressure and the quantity of atmospheric particulates (Figure II-2) show that the amount of an organic in the particulate phase in clean-air environments is rather small when the saturation-vapor pressure (P_o) is greater than 10^{-6} mm Hg. Junge (1977) suggested that most PCBs, DDT, and Hg in clean atmospheres are in the vapor phase and that compounds with saturation-vapor pressures $<10^{-7}$ mm Hg in clean air are in the particulate phase. Considering clean-, rural-, and urban-air environments, organics paving $P_o > 10^{-4}$ mm Hg should exist almost entirely in the vapor phase, and those having $P_o < 10^{-8}$ mm Hg should exist almost entirely in the particulate phase. In reality, the high-molecular-weight organic pollutants fall somewhere between these extremes, and their distribution and atmospheric lifetimes depend largely on the particulate content of air. Table II-1 gives a representative series of vapor pressures reported for selected trace organics.

Unfortunately, sampling techniques for airborne organics cannot adequately distinguish vapor from particulate-phase species. The most commonly used collection system employs a high-volume sampler with particulates collected on a glass-fiber filter and gases collected by a following adsorbent bed. The adsorbents used in the collection of atmospheric PCBs are polyurethane foam-PUF (Simon and Bidleman 1979; Bidleman and Olney 1974b) and XAD-2 macroreticular resin (Doskey and Andren 1979; Hollod GJ,

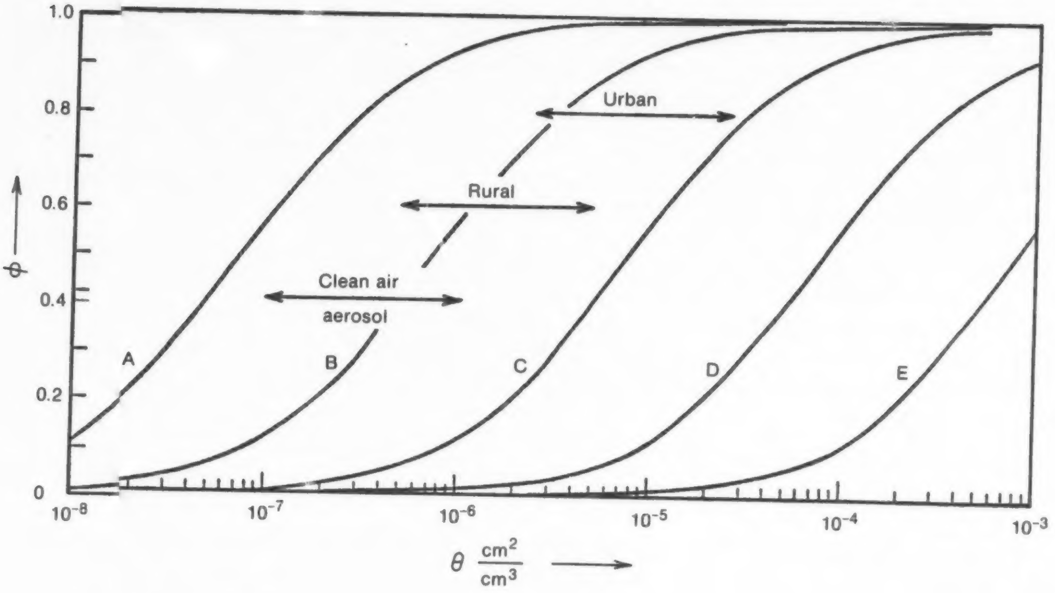


Figure II-2. Vapor-aerosol distributions of Hg calculated from vapor pressure and the quantity of atmospheric particulates. Ratio $\phi = \frac{\text{adsorbed on aerosol}}{\text{total concentration}}$ of compounds as a function of saturation vapor pressure P_o and aerosol surface θ (after Junge 1977).

A: $P_o = 10^{-8}$ mm Hg; B: $P_o = 10^{-7}$; C: $P_o = 10^{-6}$; D: $P_o = 10^{-5}$; E: $P_o = 10^{-4}$.

Eisenreich SJ, unpublished observations). The high-volume collection of airborne organics employing the filter/adsorbent system may underestimate the actual proportion of particle:phase organics because organics may be desorbed from the particles collected on the filter and the resultant vapor retained by the solid adsorbent. Nevertheless, fractions of "filter-retained" organics determined using high-volume samples consist of higher molecular-weight and low-vapor-pressure species. This was demonstrated by Cautreels and vanCauwenberghe (1978) for a homologous series of alkanes collected in the urban atmosphere. As shown in Table II-2, a significant fraction in the particle phase increases with increasing molecular weight and decreasing P_o.

Also a fraction of other high-molecular-weight species, such as PAH and phthalate esters, exist in the gas phase, even in urban atmospheres (Giam et al. 1980). Therefore, the distribution of trace organics between the glass-fiber filter and the solid adsorbent cannot be taken as unequivocal evidence of vapor/particle partitioning, but rather the sum as the total atmospheric

Table II-1. Vapor Pressures of Trace Organic Compounds

Compound	Molecular weight	mm Hg	Atm	Reference
Aroclor 1242	258 (3-Cl)	4.06×10^{-4}	5.33×10^{-7}	MacKay and Wolkoof (1973)
1248	293 (4-Cl)	4.94×10^{-4}	6.50×10^{-7}	Ibid.
1254	328 (5-Cl)	7.71×10^{-5}	1.01×10^{-7}	Ibid.
1260	373 (6.3-Cl)	4.05×10^{-5}	5.33×10^{-8}	Ibid.
2',3,4-PCB	258	1.2×10^{-4}	1.6×10^{-7}	Westcott J, Bidleman TF, unpublished observations
p,p'-DDT	356	1×10^{-7}	2.8×10^{-10}	MacKay and Wolkoff (1973)
-hexachlorocyclohexane	291	9.4×10^{-6}	1.2×10^{-8}	Ibid.
Dieldrin	377	1×10^{-7}	2.8×10^{-10}	Ibid.
Aldrin	363	6×10^{-6}	7.9×10^{-9}	Ibid.
Chloroterpenes (Strobane)	412	3×10^{-7}	8.4×10^{-10}	Melnikov (1971)
Chlorobenzene	113	1r.9	1.6×10^{-2}	MacKay et al. (1979)
Benzene	78	95	1.25×10^{-1}	Ibid.
Toluene	92	28.4	3.7×10^{-2}	Ibid.
Ethyl benzene			1.25×10^{-2}	Ibid.
Naphthalene	128	0.09	1.2×10^{-4}	MacKay et al. (1979)
Biphenyl			2.86×10^{-3}	Calculated from data of MacKay et al. (1979)
Acenaphthalene			5.74×10^{-2}	
Phenanthrene			5.07×10^{-5}	
Pyrene	202	6.8×10^{-6}	9×10^{-9}	Pupp et al. (1974)
Benzo(a)pyrene	228	6.6×10^{-7}	9×10^{-10}	Ibid.
Diethylhexylphthalate		10^{-7}	10^{-10}	Ibid.

Table II-2. Apparent Particulate- and Gas-Phase Distributions for Organics in Urban Air

Compound	Particulate (ng m^{-3})	Gas (ng m^{-3})	P/G ratio
Hydrocarbons			
n-C_{15}	--	61	--
n-C_{17}	--	66.5	--
n-C_{19}	0.8	15.1	0.053
n-C_{22}	2.33	4.23	0.55
n-C_{25}	9.50	5.74	1.66
n-C_{29}	15.8	6.56	2.4
PAHs			
Phenanthrene + anthracene	1.21	44.7	0.027
Fluoranthene	2.22	8.52	0.26
Pyrene	1.64	3.36	0.488
Benzo(a)anthracene + chrysene	12.2	3.87	3.15
Benzo(a)fluoranthene	23.1	2.01	11.5
Benzo(a)-, benzo(e) + perylene	20.1	2.69	7.47
di-isobutylphthalate	1.73	32.8	0.053
di-n-butylphthalate	101	353	0.286
di-2-ethylhexyl phthalate	54.1	127	0.426

SOURCE: Cautreels and vanCauwenberghe (1978).

Table II-3. Ranges of Gas-Particle Distribution Factors for Organics (f_c), Nitrates (f_n), and Sulfates (f_s) in Pasadena, CA

Day	f_c	f_n	f_s
7/12/73	0.009-0.03	0.012-0.018	0.230-0.333
7/25/73	0.009-0.062	0.019-0.068	0.13-0.39
10/17/73	0.007-0.024	0.007-0.032	0.171-0.466

SOURCE: Adapted from Grosjean and Friedlander (1975).

NOTE: $$f_c = \frac{OC_p}{HC_g + OC_p}, \quad f_n = \frac{NO_3^-}{NO_x + NO_3^-}, \quad f_s = \frac{SO_4^=}{SO_2 + SO_4^=}$$

concentration. This observation also points out the importance of using an additional adsorbent as a back-up to the filter to prevent the loss of the volatile fraction of the organics.

Using similar methodologies, Grosjean and Friedlander (1975) found that 97%-99.3% of organic carbon, 93%-99.3% of nitrogen, and 53%-87% of sulfur in Pasadena air consisted of vapor-phase components (Table II-3). There is also a controversy about whether atmospheric PCBs exist in the vapor or particle phase. The data in Table II-4, summarizing some determinations in urban and marine and rural environments, show that ~85%-100% of airborne PCBs are, at least operationally, in the vapor phase. Junge (1977) presented vapor pressure and adsorption evidence that ~90% of PCBs are in the vapor phase. Thus, for many trace organics, the vapor phase may contribute a sizeable fraction of the atmospheric concentration.

The particle size with which trace pollutants are associated is largely unknown. Doskey and Andren (1980) showed that PCBs are probably associated with 0.1 to 1.0 μm particles. Van Vaeck and vanCauwenberghe (1978) showed that aerosol PAH in urban, rural, and coastal environments have mass-median diameters (mmd) of 0.7-1.6 μm with 34%-70% of the mass occurring in sizes less than 1 μm (Table II-5). Because of their higher surface:volume ratio and higher organic content, submicron particles have higher concentrations than do larger particles. However, Van Vaeck and vanCauwenberghe (1978) found that a significant fraction of the

Table II-4. Particulate- and Vapor-Phase Distributions for Atmospheric PCBs

Location	Percentages Particulate	 Vapor	Reference
Marine and Rural			
Atlantic	10	90	Junge (1975)
North Atlantic	2	98	Bidleman and Olney (1974a)
Grand Banks, Newfoundland	1	99	Harvey and Steinhauer (1974)
Gulf of Mexico	1	99	Giam et al. (1980)
Lake Superior	0	100	Eisenreich and Hollod (1980)
Lake Michigan	3	97	Doskey (1978)
Bermuda	2	98	Bidleman and Olney (1974b)
Urban			
Toronto, ON	14-43	57-86	Gilbertson (1976)
Hamilton, ON	5-18	82-95	Ibid.
Milwaukee, WI	16	84	Doskey (1978)
Lake Michigan (Chicago)	13	87	Murphy and Rzeszutko (1977)
Sheridan Park, ON	11	89	Gilbertson (1976)
Columbia, SC	8	92	Bidleman and Christensen (1979)
Chicago, IL	4	96	Murphy and Rzeszutko (1977)

Table II-5. Particle-Size Distributions for PAHs in Ambient Aerosols in Urban, Rural, and Coastal Areas

Compound	Coastal		Rural		Urban	
	< 1 μm (%)	mmd (μm)	< 1 μm (%)	mmd (μm)	< 1 μm (%)	mmd (μm)
Phenanthrene and anthracene	49	1.1	36	1.5	47	1.1
Fluoranthene	46	1.1	39	1.4	60	0.8
Benzo(a)anthracene and chrysene	57	0.9	54	0.9	67	0.7
Benzo(b + k) fluoranthenes	64	0.7	63	0.8	70	0.7
Benzo(a + e) pyrenes	64	0.7	58	0.9	68	0.7
Dibenzo anthracenes	61	0.8	34	1.6	59	0.8

SOURCE: Van Vaeck and vanCauwenberghe (1978).

high-molecular-weight n-alkanes, carboxylic acids, and PAHs were associated with particles >1 μm mmd. Since these particles have higher deposition velocities and washout ratios (Slinn et al. 1978), the flux of high-molecular-weight organics may be dominated by the deposition of large particles. That is, even though most trace organics are on submicron particles, most of those deposited may be due to large particles.

3. TRANSFER OF GASES ACROSS AIR/WATER INTERFACE

Transfer of gases across the air/water interface can be predicted from a two-film diffusion model (Liss and Slater 1974). In this model, the air and water reservoirs are assumed to be well mixed except for thin, stagnant films of air and water at the interface. The rate of transfer is governed by the molecular diffusion across these interfacial layers and driven by the concentration gradients between equilibrium concentrations at the interface and the concentrations in the bulk air and in water reservoirs. For the steady-state transfer across air and water films, the flux (F) is given by (MacKay et al. 1979):

and

$$F = K_{OL}\ (C - P/H)$$
$$1/K_{OL} = 1/K_L + RT/HKg \qquad (3\text{-}1)$$

where F is the flux (mol m^{-2} h^{-1}); K_L and Kg, the liquid and gas-phase mass-transfer coefficients (m h^{-1}); K_{OL}, the overall liquid-phase mass-transfer coefficient (m h^{-1}); H, the Henry's law constant (atm m^3 mol^{-1})(P/C); C, the solute concentration in the liquid phase (mol m^{-3}); P, the solute partial pressure (atm); T, the absolute temperature (K); and R, the gas constant (m^3 atm mol^{-1} K^{-1}).

3.1 Resistance to Air/Water Interface

Resistance to gas-phase transfer occurs in both the liquid and gas films. For solutes of increasing molecular weight, both K_L and Kg decrease although their ratio may remain approximately the same. MacKay et al. (1979) have shown that for $H > 5 \times 10^{-3}$ atm m^3 mol^{-1}, resistance lies almost totally in the liquid phase; the flux is then described by

$$F = K_L\ (C - P/H). \qquad (3\text{-}2)$$

If $H < 5 \times 10^{-6}$ atm m^3 mol^{-1}, then resistance lies almost totally in the gas phase; the flux can be described by

$$F = \frac{KgH(C-P/H)}{RT} \qquad (3\text{-}3)$$

For H values between these extremes, resistance to mass transfer occurs in both the gas and liquid film; the equation for flux is

$$F = K_{OL}\ (C-P/H). \qquad (3\text{-}4)$$

A knowledge of the Henry's law constant is essential to predicting air/water exchange because one must be able to calculate the concentration of the organic compound in the water in equilibrium with the organic in the vapor phase. If the water is undersaturated with respect to equilibrium with the atmosphere (negative C-P/H in Eqs. 3-2, 3-3, and 3-4), there will be a net transport of vapor to the water. If the water is oversaturated with respect to the air (positive C-P/H), there will be a net transport of vapor to the atmosphere. The rate and amount of material transferred depends on whether the compound is liquid- or gas-phase controlled. This can be determined from the equations above.

Henry's law constant is calculated by dividing the solute vapor pressure at saturation (25°C) and the solute solubility

Table II-6. Water Solubilities of Trace-Organic Compounds

Compound	Solubility (mol m^{-3})	Reference
Aroclor 1242	9.3×10^{-4}	MacKay and Wolkoff (1973)
1248	1.8×10^{-4}	Ibid.
1254	3.7×10^{-5}	Ibid.
1260	7.2×10^{-5}	Ibid.
p,p'-DDT	3.4×10^{-6}	Ibid.
HCH	2.5×10^{-2}	Ibid.
Dieldrin	6.6×10^{-4}	Ibid.
Aldrin	5.5×10^{-4}	Ibid.
Chloroterpenes (strobane)	1.2×10^{-3}	Ibid.
Chlorobenzene	4.2	MacKay et al. (1979)
Benzene	22.8	Ibid.
Toluene	5.7	Ibid.
Naphthalene	0.24	Ibid.
Biphenyl	4.9×10^{-2}	Ibid.

(25°C) in water. Recently, direct measurements of H for relatively low-molecular-weight organics were made by stripping organic vapors from an aqueous solution using a gas stream (MacKay et al. 1979). The calculated values based on saturation vapor pressures and solubilities (Tables II-1 and II-6) agree well with experimentally determined values (Table II-7). Unfortunately, one (or both) of these physical constants is not accurately known for most high-molecular-weight organic pollutants because of the difficulties of working with slightly soluble organics. Furthermore, the true "dissolved" aqueous concentration in equilibrium with the atmospheric species needs to be known.

Vapor pressures for PCBs have been determined at high temperatures and estimated values at 25°C have been obtained by extrapolation using the Antoine equation (MacKay and Wolkoff 1973). However, these values are uncertain and possibly 10^1 to

Table II-7. Henry's Law Constants

Compound	Henry's law constant (atm m^3 mol^{-1})		Controlling phase (gas/liquid)
	Calculated	Measured	
Aroclor 1242	5.7×10^{-4}	$1.1 \times 10^{-6} - 1.4 \times 10^{-7}$*	G
1248	3.6×10^{-3}		
1254	2.7×10^{-3}	$2.9 \times 10^{-7} - 6.9 \times 10^{-8}$*	G
1260	7.4×10^{-4}		
2',3,4-PCB	5.3×10^{-4}		G,L
p,p'-DDT	8.2×10^{-5}		G,L
HCH	4.8×10^{-7}		G
Dieldrin	4.2×10^{-7}		G
Aldrin	1.4×10^{-5}		G,L
Chloroterpenes	7×10^{-7}		G
Chlorobenzene	3.8×10^{-3}	3.8×10^{-3}	L
Benzene	5.5×10^{-3}	5.6×10^{-3}	L
Toluene	6.5×10^{-3}	6.6×10^{-3}	L
Naphthalene	5×10^{-4}	4.8×10^{-4}	G,L
Biphenyl		4.1×10^{-4}	G,L
Acenaphthalene		1.5×10^{-4}	G,L
Phenanthrene		3.9×10^{-5}	G,L

SOURCE: Experimental values of H (except as noted) from MacKay et al. (1979).

NOTE: For $H < 5 \times 10^{-6}$, > 95% G; for $H > 5 \times 10^{-3}$, > 95% L.

*Air/water partition coefficients determined in natural lake water (Doskey and Andren 1980).

10^3 too high. Saturation vapor pressures of individual PCB isomers should be much higher above commercial liquid mixtures than above a pure solid, which is the physical form of individual isomers. Recently water solubilities were reported for pure PCB isomers in distilled water and seawater (Dexter and Pavlou 1978), and the vapor pressure of a trichlorobiphenyl isomer was measured (Westcott J, and Bidleman TF, unpublished observations).

3.2 Problems

Thus, vapor-phase trace organics partition into water and can be described, in part, by the Henry's law constant (Table II-7). In theory, if H is known, then the concentration of a trace organic at equilibrium in air and water can be calculated. However, in practice, the situation is more complex. For example, vapor-phase PCBs entering the water column may remain dissolved and unassociated, bind with dissolved or colloidal organics, adsorb onto a particle surface, or be absorbed into an organic particle. Only the dissolved, unassociated form equilibrates with the organic vapor in the atmosphere. To determine whether the organics present as vapor in air are in equilibrium with the organics in water, the concentration of the dissolved species must be known. Analytically, this measurement is, at best, difficult to perform at the ambient concentrations observed in the environment--1 to 10×10^{-9} g ℓ^{-1}. This problem might be avoided by measuring the concentration on suspended particulate matter and applying a particulate/water-distribution coefficient, such as that determined by Chen et al. (1980), Karickoff et al. (1979), and Dexter and Pavlou (1978).

4. WET REMOVAL OF TRACE ORGANICS FROM THE ATMOSPHERE

Wet removal of airborne trace organics occurs by scavenging of particles and vapor partitioning. The relative importance of these processes depends on the fraction of organic present as an aerosol and the particle-size distribution of the particulates and on H for vapor-phase partitioning. A falling raindrop should attain equilibrium with a trace-organic vapor in ~10 m (Slinn et al. 1978). Washout ratios calculated as the reciprocal of H are given in Table II-8 along with the field values calculated as

$$W = \frac{\text{mass organic } \ell_{\text{rain}}^{-1}}{\text{mass organic } \ell_{\text{air}}^{-1}} .$$

For PCBs and DDT, the field values are much higher than predicted for values from vapor partitioning into rain. This suggests that wet removal of PCBs and DDT occurs predominantly by scavenging of

Table II-8. Washout Ratios for Trace-Organic Compounds

Compound	Vapor calculation	Field measurement	Reference
Aroclor 1242	43	1.2×10^4	Murphy and Rzeszutko (1977)
	$2.2 \times 10^4 - 1.7 \times 10^5$		Doskey and Andren (1980)
1248	6.8	8.6×10^4	
1254	9.0	8.6×10^4	Murphy and Rzeszutko (1977)
	$8.4 \times 10^4 - 3.5 \times 10^5$	7.8×10^4 1.9×10^4	Bidleman and Christensen (1979) Giam et al. (1978)
1260	33		
2',3,4-PCB	46		
p,p'-DDT	298	5.4×10^4 7.4×10^4 1.9×10^4	Atkins and Eggleton (1974) Bidleman and Christensen (1979) Giam et al. (1978)
p,p'-DDE		$2.5 \times 10^3 - 1.5 \times 10^4$	Giam et al. (1980)
-hexachloro-cyclohexane	5.1×10^4	$5 \times 10^3 - 1 \times 10^4$ $1.3 - 3.4 \times 10^4$	Atkins and Eggleton (1974) Giam et al. (1978)
Dieldrin	5.8×10^4	2×10^3 $2 \times 10^3 - 9 \times 10^3$	Atkins and Eggleton (1974) Giam et al. (1980)
Aldrin	1.7×10^3		
Chloroterpenes	3.5×10^4	$< 7 \times 10^3 - 3 \times 10^5$	Bidleman and Christensen (1979)
Chlorobenzene	6.4		
Chlordane		7×10^3 4×10^3	Bidleman and Christensen (1979) Giam et al. (1980)
Hexachloro-benzene	370	$>1.5 \times 10^3$	Giam et al. (1978)
Naphthalene	49		
Phenanthrene	626		
Diethylhexylphthalate		$1.4 \times 10^4 - 8.5 \times 10^4$	

particulate matter. For other high-molecular-weight organics, vapor scavenging may be important. This overall behavior is supported by findings that early portions of rainfall are high in particulates and PCBs (Murphy and Rzeszutko 1977; Strachan and Huneault 1979). However, as with air/water vapor exchange, the accuracy of these predictions depends on the accuracy of H.

5. DRY DEPOSITION OF PARTICULATES

The dry deposition to a receptor surface of trace organics associated with atmospheric particulates depends on the type of surface, the resistance to mass transfer in the deposition layer, and the particle size and concentration. Ideally,all these factors should be known to adequately describe the transfer of atmospheric particulates to a surface. For particles with radii a in the range of $0.001 < a < 0.1$ μm, the transfer velocity can be given by (Slinn et al. 1978)

$$k_D \sim \frac{h(u_*)a}{(Sc)a^{2/3}} , \qquad (5\text{-}1)$$

where h is von Harmon's constant (~0.4), u_* the friction velocity, and Sc the Schmidt number.

For large particles, transfer ratios increase, especially above 1.0 μm. In practical terms, the deposition of particles to a surface can be described by

$$F = V_d(C) , \qquad (5\text{-}2)$$

where F is the flux, V_d the deposition velocity, and C the concentration. The V_d depends primarily on the deposition surface (i.e., water versus forest canopy) and particle size. Deposition velocities are minimal for particles in the range $0.1 < a < 1.0$ μm and increase for both larger and smaller particles. For particles having radii in the range of 2-10 μm, V_d is ~1-5 cm s^{-1}; for particles having radii < 0.1 μm, V_d is ~0.02-0.8 cm s^{-1}; and for particles in the range of 0.1-1.0 μm, V_d is ~0.1-1 cm s^{-1} (see Part III). Slinn and Slinn (1980) proposed that deposition of submicron particles to a water surface may be enhanced by rapid particle growth from water condensation in the deposition layer. Organic pollutants, especially those with low vapor pressures, that have high molecular weight and are hydrophobic in nature are associated with particles above and below one micron, with a slight preference for the smaller particles (Table II-5). Many organics condense on aerosol surfaces following emission from a high-temperature source. Because of the nonpolar nature of most trace organics, the organic carbon content of the particle is also important.

Deposition velocities are given in Table II-9 for various airborne-organic species. An average V_d for trace organics in the atmosphere has been determined by measuring the flux to a surface coated with glycerol, ethylene glycol, and mineral oil or a plain, wet filter paper and simultaneously measuring the atmospheric concentrations of the compound of interest. For surfaces coated with mineral oil or another nonpolar substrate, it is difficult to determine whether the organic flux is due only to particle deposition or to a combination of gas and particle flux (Murphy et al. 1980). The deposition velocities determined in this way ($V_d = F/C_{air}$) are operational in nature but may represent realistic estimates of actual total dry flux to a water surface if polar, hygroscopic coatings are used.

6. SOURCES OF TRACE ORGANICS TO THE ATMOSPHERE

6.1 Sources I

The sources of many trace organics to the atmosphere are obvious, but it may prove useful to briefly describe the important types of sources. Most trace organics in the atmosphere occur in three categories: (1) compounds such as the volatile freons with high vapor pressures, which upon use accumulate in the air; (2) compounds such as pesticides and herbicides which are often injected into the atmosphere by spraying and also evaporate from plant surfaces; (3) compounds formed by combustion, such as PAHs, which are discharged directly to the atmosphere. The vapor pressures of high-molecular-weight PAHs preclude their being in the atmosphere without originating from a high-temperature source.

Some compounds enter the atmosphere by a variety of sources. Solvents, plasticizers, etc., that are exposed to air enter the atmosphere by vaporization. Natural organic compounds produced by vegetation, such as terpenes, evaporate from forest canopies. Open burning, such as forest and brush fires, causes many organic compounds to be emitted into the air, both as particulates and vapors. The incomplete combustion of municipal refuse, sewage sludge, and industrial products results in the emission of large quantities of organics.

Murphy and Rzeszutko (1977) stated that high-temperature sources such as these may be responsible for much of the PCBs "recently" added to the environment. PAHs either formed in or, at least, emitted by the combustion of fossil fuels condense on aerosols and can be transported great distances.

Table II-9. Dry-Deposition Velocities

Compound	Deposition velocity ($cm\ s^{-1}$)	Comment	Reference
PCB (Aroclor 1242, 1254)	0.5	Estimated from Sehmel and Sutter (1974)	Doskey and Andren (1980)
PCBs	0.3-3	Mineral-oil-coated plates	McClure (1976)
PCBs, DDT	0.19	Estimated gas phase	Bidleman et al. (1976)
PCBs, DDT	1.0	Estimated particulate	Ibid.
PCSs (Total)	0.14	Glycerol-coated plates	Eisenreich and Hollod (1980)
PCBs (Aroclor 1016)	0.04	Glycerin-water Al pans (in Columbia, SC)	Bidleman and Christensen (1979)
PCBs (Aroclor 1254)	0.43	Glycerin-water Al pans (in Columbia, SC)	Ibid.
Chlordane	0.068	Glycerin-water Al pans (in Columbia, SC)	Ibid.
p,p'-DDT	1.3	Glycerin-water Al pans (in Columbia, SC)	Ibid.
Toxaphene	0.24	Glycerin-water Al pans (in Columbia, SC)	Ibid.

6.2 Sources II

The manufacturing process and the sites of manufacturing, distribution, and use are other sources of trace organics in the atmosphere, although mostly of local significance. Much more prevalent are dispersed sources, such as landfills, dumps, and other areas, where spent or spilled organic products are disposed of. Finally, some manufacturing by-products and wastes are used as an energy source and combusted alone or with other materials. For example, the total quantity of PCBs present in waste oils, although limited to ~50 mg ℓ^{-1}, is substantial when the total amount of oil used in commerce is considered.

7. VARIABILITY OF CONCENTRATIONS AND FLUXES

One difficulty in determining concentrations of trace organics in air and precipitation and their flux to a receptor surface is variability. Concentrations and fluxes vary with airborne concentration, macrometeorology and micrometeorology, frequency, intensity and duration of precipitation, and organic speciation. This results in field values varying by an order of magnitude or more. Thus, a statistically valid number of samples needs to be taken to accurately estimate concentration. Conclusions based on a few samples or samples collected over short time periods and from similar meteorological conditions must be applied with caution.

8. ATMOSPHERIC CONCENTRATIONS

A paucity of data exists on the occurrence of trace-organic contaminants in the atmosphere. Only recently has the relative impact of atmospheric deposition on water quality (e.g., acid rain and PCBs in the Great Lakes) been recognized. Polluted air masses accumulate chemical components from local sources as well as from sources hundreds or thousands of kilometers away. Air-mass circulation can transport airborne pollutants from urban or industrialized centers, depositing them in distant regions. The published and unpublished literature over the last ten to fifteen years was reviewed to determine the nature and concentration of airborne pollutants found in rain and snow and in vapor and particle phases in urban and rural areas. The data shown in Tables II-10 and II-11 summarize our findings for a wide range of trace-organic compounds. In many instances, especially for PAHs, airborne-contaminant data were available only for aerosol concentrations determined in urban areas. Where possible, median values are identified so that values outside the median range can be more readily interpreted.

Table II-10. Atmospheric Concentrations of Trace-Organic Compounds in Urban and Rural Environments

Compound	Urban		Rural	
	V/P* ($ng\ m^{-3}$)	R/S* ($ng\ \ell^{-1}$)	V/P* ($ng\ m^{-3}$)	R/S* ($ng\ \ell^{-1}$)
Total PCBs	0.5-30 (5-10)	10-250 (50)	0.1-2 (1)	10-100 (15-50)
Total DDT (ΣDDT, DDE, DDD)	0.01-1	1-30	0.01-0.05	1-10
Dieldrin	0.5-10	5-40	0.01-0.1	0.5-30 (1-4)
Aldrin	1-10	7	0.1-1	0.5-3
Toxaphene	0.02-10 (South)	10-100 (South)	0.02-2	1-10
α-BHC	2-10	3-60	0.25-0.4	1-35 (10-20)
γ-BHC (Lindane)		1-12 (6)	0.2-4	1-15 (5)
Hexachlorobenzene		1-10	0.1-0.3	1-4
Chlordane	0.1-0.5		0.01-0.5	1-5
Heptachlor	1-20		0.2-5	1-9 (2)
Heptachlor epoxide				0.5-5 (2)
Endrin				
Methoxychlor				1-20 (8)
Trichloroethylene	100-1000		100-1000 (Alaska)	
Tetrachloroethylene	500-2500			
Mirex				<1
α-endosulfan		1-10		1-10 (2)
β-endosulfan		1-10 (3)		1-10 (2-5)
Polychlorinated naphthalenes	10-25			
Dibutylphthalate			0.5-5	
Diethylhexylphthalate			0.5-5	

NOTE: Numbers in parentheses represent median values.

*V/P = vapor/particulate, R/S = rain/snow.

Table II-11. Atmospheric Concentrations of PAHs in Different Environments

Compound	Urban V/P* (ng m^{-3})	 R/S* (ng ℓ^{-1})	Rural V/P* (ng m^{-3})	 R/S* (ng ℓ^{-1})
Benzene	600-30,000 (1,000-2,000)			
Toluene	600-50,000 (1,000-10,000)			
Anthracene	0.2-10 (0.5-4)		0.01-1.0 (0.1-0.5)	
Phenanthrene	10-50		0.02-6 (0.1-1)	
Fluoranthrene	0.1-13 (1-5)	300	0.2-7 (0.5-2)	60
Pyrene	0.2-10 (1-5)		0.1-10 (0.5-2)	
Benz(a)-anthracene	0.06-5 (0.3-3)		0.4-5 (0.1-1)	
Chrysene	0.04-5 (1-4)		0.1-12 (0.1-2)	
Benzo(k)-fluoranthene	0.06-5 (0.1-1)		0.08-4	
Benzo(a)pyrene	0.03-10 (0.3-3)		0.01-5 (0.2-2)	
Benzo(e)pyrene	0.05-5 (0.5-2)		0.02-3 (0.2-2)	
Indeno [1,2,3-c-d] pyrene	0.03-3 (0.3-2)			
Perylene	0.01-14 (0.1-1)		0.01-2 (0.1-0.6)	
1,12-benzo-perylene	1-30 (1-10)	90	0.04-3	10
Benzo(g,h,i) perylene	0.2-20 (1-10)		0.06-1.9 (0.5-2)	
Coronene	0.2-20 (1-6)		0.02-0.2	
Total PAH				50-300

NOTE: Numbers in parentheses represent median values.

*V/P = vapor + particulate, R/S = rain + snow.

Table II-12. Atmospheric Concentrations and Fluxes of PCBs in Different Environments

Location	Air		Precipitation		Fluxes
	Range (ng m^{-3})	Mean	Range (ng ℓ^{-1})	Mean	(μg m^{-2} yr^{-1})
Urban	0.5-30	5-10	10-250	50	100-700
Rural	0.12	0.8	1-50	20	50-500 (1.5)
Remote	0.02-0.5	0.1	1-30	5	0.2-20 (40)
Marine	0.02-2	0.5	0.5-10	1-5	0.1-20 (35)
Great Lakes	0.4-3	1	10-150	20-50	20-150 (4)

NOTE: Numbers in parentheses represent approximate ratios of urban-to-area fluxes.

9. TOTAL DEPOSITION IN URBAN, RURAL, AND REMOTE ENVIRONMENTS

The total fluxes (wet and dry) of airborne trace organics to urban and rural environments have been reported for remarkably few compounds. Table II-12 shows the estimated aerosol and precipitation concentrations of total PCBs and their estimated fluxes to the Great Lakes and to the urban, rural, marine, and remote environments of the world. Admittedly, some geographical areas overlap but the estimates are based on concentrations and, in some cases, the fluxes were actually observed in the respective areas. It is useful to compare the fluxes estimated for urban areas with those estimated for the Great Lakes and the rural, marine, and remote environments. The ratio of urban PCB fluxes to remote and marine fluxes is ~40, to the Great Lakes ~4, and to rural areas near urban centers ~1.5. Waters in the respective areas also show levels of contamination in the order of their increasing input ratio. On the basis of calculations made by Bidleman and Olney (1974b), total DDT inputs ought to be ~10^1 less than inputs for PCBs but relative ratios should remain approximately constant.

Table II-13 shows the fluxes of selected chlorinated hydrocarbons estimated for rural areas and based on the following criteria: (1) dry-deposition velocities for gases and submicron particles are ~0.1-1.0 cm s^{-1} (see Part III) and (2) wet fluxes from rain and snow concentrations and precipitation intensities are 70 or 100 cm yr^{-1}. These values are typical for the upper

Table II-13. Atmospheric Fluxes of Trace-Organic Compounds to Rural Environments

Compound	Dry				Wet				Ratio of wet:dry flux V_d=0.1 cm s^{-1} P_o=70 cm yr^{-1}
	Concentration		Flux		Concentration		Flux		
	Range (ng m^{-3})	Mean	0.1 (cm s^{-1}, μg m^{-2} yr^{-1})	1.0	Range (ng ℓ$^{-1}$)	Mean	70 (cm yr^{-1}, μg m^{-2} yr^{-1})	100	
Total PCB	0.1-2	1	32	315	15-50	25	18	25	0.56
Total DDT	0.01-0.05	0.03	1	9.5	1-10	5	3.5	5	3.5
Dieldrin	0.01-0.1	0.05	1.6	16	1-4	2	1.4	2	0.88
Aldrin	0.1-1	0.5	16	160	0.5-3	2	1.4	2	0.09
Toxaphene	0.02-2	0.5	16	160	1-10	5	3.5	5	0.22
α-BHC (Lindane)	1-4	2	63	630	1-15	8	5.6	8	0.13
Hexachlorobenzene	0.1-0.3	0.2	6.3	63	1-4	2	1.4	2	0.22
Chlordane	0.01-0.5	0.1	3.2	32	1-5	2	1.4	2	0.44
Heptachlor	1-5	2	63	630	1-9	3	2.1	3	0.03
Dibutylphthlate	0.5-5	2	63	630	4-40*	10	7	10	0.11
Diethylhexylphthalate	5-5	2	63	630	4-40*	10	7	10	0.11
Total PAHs	10-100	20	630	6300	50-300	100	70	1000	0.11

NOTE: For dry flux, $\mu g\ m^{-2}\ yr^{-1} = V_d\ (cm\ s^{-1})\ (3.15 \times 10^7\ s\ yr^{-1})\ (\frac{1\ m}{10^2\ cm})(\frac{10^{-3}\ \mu g}{ng})(Conc.\ ng\ m^{-3})$;

for wet flux, $\mu g\ m^{-2}\ yr^{-1} = (Conc.\ ng\ \ell^{-1})(\frac{10^3 \ell}{m^3})(m\ yr^{-1})(\frac{10^{-3} \mu g}{ng})$.

*Estimated from $W = 10^5$ for Concentration = 0.5-5 ng m^{-3}.

Midwest at the western boundary of the Great Lakes (70 cm yr^{-1}), increasing eastward to the United States Atlantic coast (100 cm yr^{-1}). In some cases trace-organic concentrations in precipitation were estimated from washout ratios (W) of $\sim10^5$. These numbers represent the maximum input for Midwest and East Coast areas in urban and industrial zones. An adjustment may be required for other areas.

The atmospheric fluxes of trace organics listed in Table II-13 are only estimates based on the available data base, which is small. They are probably accurate by an order of magnitude only and should be construed to represent ranges for researchers and governmental agencies to use. One question often posed is, what is the relationship between wet and dry fluxes? Using conservative estimates for both dry (V_d = 0.1 cm s^{-1}) and wet fluxes (P_o = 70 cm yr^{-1}), the values in the last column of Table II-13 suggest that dry deposition exceeds wet deposition by 1 to 5 times. This is in contrast to atmospheric metal fluxes, which are about evenly divided between wet and dry deposition (Parts I and III).

10. APPLICATIONS OF FLUX CALCULATIONS: ATMOSPHERIC PCB INPUT TO THE GREAT LAKES

The deposition of atmospheric organics to water bodies can logically be separated into dry and wet deposition. The processes affecting deposition and the various theoretical or empirical approaches to estimating atmospheric fluxes have already been discussed. Thus, a relatively large body of information exists on the processes controlling PCB deposition to water surfaces and the environmental distribution of PCBs. For these reasons, the flux of PCBs from the atmosphere to the Great Lakes was estimated as an example of a general approach to the problem. The Great Lakes were selected because they contain the greatest degree of fish contamination not related to a specific source. For example, most game and commercial fishes in Lake Michigan, part of which is in the industrialized region of northern Indiana and Chicago, Illinois, show significant accumulations of PCBs (>2 ppm). Although Lake Superior is in a forest-dominated watershed, PCBs in fish are commonplace. This supports the postulate that PCBs are distributed over long distances by atmospheric transport and deposition.

10.1 Dry Deposition

The dry deposition of particulate matter has been estimated using the following equation:

$$F = V_d(C_{air\ part}), \qquad (10\text{-}1)$$

where F is the flux (ng m^{-2} s^{-1}); V_d, the dry-deposition velocity (m s^{-1}); and $C_{air\ part}$, the concentration in atmospheric particulate matter (ng m^{-3}). Available data suggest that ~5%-15% of the atmospheric PCBs in the particulate phase (Table II-14) are associated with submicron-size particles and have V_d values of 0.001-0.005 m s^{-1}. By using $C_{air\ part}$ = 0.13 and 0.15 ng m^{-3}, respectively, for Lakes Michigan (Doskey 1978) and Superior (Eisenreich and Hollod 1980) and V_d values of 0.005 (Doskey and Andren 1980) or 0.0013 m s^{-1} (Hollod 1979), the dry particle PCB flux may be calculated as ~20-22 μg m^{-2} yr^{-1}.

The dry deposition of vapor-phase PCBs directly to a water surface is estimated from (MacKay et al. 1979)

$$F = K_{og} \left[\frac{CH-P}{RT}\right] , \qquad (10\text{-}2)$$

where F is the flux (mol m^{-2} h^{-1}); K_{og}, the overall gas-phase mass-transfer coefficient (m h^{-1}); C, the PCB concentration in dissolved phase in water (mol m^{-3}); H, the Henry's law constant (atm m^3 mol^{-1}); P, the atmospheric partial pressure of PCB (atm); and RT, the gas constant times absolute temperature (m^3 atm^{-1} mol^{-1}).

By assuming gas-phase control for PCB transfer across the air/water interface (Doskey and Andren 1980; MacKay et al. 1979) and applying the parameters in Table II-14, the vapor-phase flux was estimated as ~2800 kg yr^{-1} (~48 m^{-2} yr^{-1}) and 6000 kg yr^{-1} (~73 μg m^{-2} yr^{-1}) for Lake Michigan and Lake Superior, respectively (Table II-15). The higher PCB-vapor flux to Lake Superior is primarily a consequence of the higher atmospheric concentration and higher relative percentage assumed in the gas phase (~90%). Gas-phase control for PCB transfer across the air/water interface was based on the Henry's law constant (10^{-6}-10^{-7} atm m^3 mol^{-1}) and arguments presented by Doskey and Andren (1980).

10.2 Wet Deposition

Wet deposition is calculated for gas scavenging by

$$F = \alpha(P_o)C_b, \qquad (10\text{-}3)$$

where F is the flux (ng m^{-2} yr^{-1}); α, the PCB-vapor washout

Table II-14. Parameters for PCB Flux to the Great Lakes

	Lake Michigan		Lake Superior	
	1242	1254	1242	1254
Concentration in air				
Vapor (atm)	5.6×10^{-14}	1.5×10^{-4}	7.9×10^{-14}	1.8×10^{-14}
(ng m^{-3})	0.87		1.35	
Particulate (ng m^{-3})	0.13		0.15	
Concentration in water (mol m^{-3})	7.7×10^{-9}	2.6×10^{-8}	3.8×10^{-9}	3.1×10^{-9}
Aerosol-deposition velocity (m s^{-1})	0.005		0.0013	
Air/water partition coefficient (atm m^3 mol^{-1})	2.8×10^{-7}	1.4×10^{-7}	1.4×10^{-7}	6.9×10^{-8}
Overall gas-phase mass-transfer coefficient (K_{og})(m h^{-1})	7.9	7.0	7.9	7.0
RT (25°C)	2.45×10^{-2}		2.45×10^{-2}	
Surface area (m^2)	5.9×10^{10}		8.21×10^{10}	

SOURCE: For Lake Michigan parameters, Doskey and Andren (1980); for Lake Superior parameters, Eisenreich and Hollod (1980).

Table II-15. Atmospheric Flux of PCBs to the Great Lakes (kg yr^{-1})

	Lake Michigan	Lake Superior	
	Calculated	Calculated	Measured
Dry deposition			
Particulate	1,200	70-2,900	5,100
Vapor	2,800	6,000	
Wet deposition	5,000	2,800-3,600	1,500-3,000
Total input	9,000	8,900-12,500	6,600-8,300

SOURCE: For Lake Michigan values, Doskey and Andren (1980), and (wet deposition), Murphy and Rzeszutko (1977); for Lake Superior values, Eisenreich and Hollod (1980).

NOTE: Dry deposition: flux = $V_d(C_{air})$;

wet deposition: flux = $C_{rain}(P_o)$.

coefficient (H^{-1}); P_o, the rainfall intensity (m yr^{-1}); and C_b, the vapor phase concentration (ng m^{-3}) at a reference height above the water surface. The washout of particles containing PCB can be calculated from the following:

$$F = W(P_o)C_b \ , \qquad (10\text{-}4)$$

where F is the flux (ng m^{-2} yr^{-1}); W, the PCB-particle washout coefficient; and C_b, the particle-phase concentration of PCB at a reference height above the receptor surface (ng m^{-3}). The values of α and W have been empirically derived or measured. However, Murphy and Rzeszutko (1977, 1978) and Eisenreich and Hollod (1980) determined the wet flux from

$$\text{Flux} = C_{rain}(P_o) \qquad (10\text{-}5)$$

where C_{rain} is the total volume-weighted PCB concentration in rain (μg m^{-3}) and P_o, the rainfall or snowfall intensity (m yr^{-1}) such that flux has units of μg m^{-2} yr^{-1}.

Eisenreich and Hollod also derived values for W and α from data provided by Slinn et al. (1978). Wet-flux rates varied from $\sim$85 μg m^{-2} yr^{-1} for Lake Michigan to $\sim$27-34 μg m^{-2} yr^{-1} for Lake Superior (Table II-15).

In addition, Eisenreich and Hollod (1980) have estimated loadings to Lake Superior by experimentally determining a V_d value, calculating total dry flux, and estimating wet loadings based on rain and snow concentrations of 25-50 μg ℓ^{-1}.

The relative importance of the atmospheric input of PCBs to the Great Lakes compared with other sources is great. Approximately 85%-90% of the total input to both lakes is deposited from the atmosphere (Doskey and Andren 1980, Doskey 1978, Eisenreich and Hollod 1980, Hollod 1979).

11. RESEARCH RECOMMENDATIONS

The following recommended research is necessary to relieve the paucity of data that exists on trace organics in the atmosphere and their deposition and effects.

(1) Methods must be developed to distinguish between vapor- and particulate-phase, high-molecular-weight organics in the atmosphere.
(2) The relationship between the mass median diameter, the deposition velocity, and the receptor surface for atmospheric particles must be established.
(3) The size distribution of atmospheric particulates containing high-molecular-weight organics must be determined.
(4) Collection methods for dry deposition of particulate- and vapor-phase organics should be developed since this is an important fraction of total deposition.
(5) The collection efficiency of different receptor surfaces for particulate- and vapor-phase organics must be determined.
(6) Accurate data on vapor pressures and water solubilities of slightly soluble, high-molecular-weight organics need to be developed.
(7) The fugacities (true dissolved fraction) of trace organics in water need to be developed.
(8) The trace-organic compositions of rain and snow and of the aerosol and gas phases in the atmosphere need to be determined before accurate deposition rates and ecological or health impacts can be evaluated.

12. REFERENCES

Atkins DHF, Eggleton EEJ. 1974. Studies of atmospheric washout and deposition of -BHC, dieldrin, and p, p'-DDT using radiolabelled pesticides. In: Nuclear Techniques in Environmental Pollution, 521, International Atomic Energy Agency, Vienna.

Bidleman TF, Christensen EJ. 1979. Atmospheric removal processes for high molecular weight organochlorines. J. Geophys. Res. 84:7857.

Bidleman TF, Olney CE. 1974a. Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. Science 183:516.

_____. 1974b. High-volume collection of atmospheric polychlorinated biphenyls. Bull. Environ. Contam. Toxicol. 11:442.

Bidleman TF, Rice CP, Olney CE. 1976. High molecular weight chlorinated hydrocarbons in the air and sea: Rates and mechanisms of air/sea transfer. In: Marine Pollutant Transfer, Windom H, Duce RA, eds., Heath & Co., Lexington, MA.

Cautreels W, vanCauwenberghe K. 1978. Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase. Atmos. Environ. 12:1133.

Chen PH, Shieh HH, Gaw JM. 1980. Determination of PAH in airborne particulates at various locations in Taipei city by GC/MS and glass capillary GC. In: Abstracts of American Chemical Society Meeting, Houston, Texas, 60.

Clayton JR, Jr, Pavlou SP, Breitner NF. 1972. Polychlorinated biphenyls in coastal marine zooplankton: Bioaccumulation by equilibrium partitioning. Environ. Sci. Technol. 11:676.

Dexter RN, Pavlou SP. 1978. Mass solubility and aqueous activity coefficients of stable organic chemicals in the marine environment: PCBs. Marine Chem. 6:41.

Doskey PV. 1978. Transport of airborne PCBs to Lake Michigan. Thesis, University of Wisconsin, Madison.

Doskey P, Andren AW. 1979. High-volume sampling of airborne PCBs with Amberlite XAD-2. Anal. Chim. Acta, 110:129.

Doskey PV, Andren AW. 1980. Modeling the flux of atmospheric PCBs across the air/water interface. Environ. Sci. Technol. (in press).

Eisenreich SJ, Hollod GJ. 1980. Atmospheric input of PCBs to the Great Lakes; impact on the Lake Superior ecosystem. In: Atmospheric Input of Pollutants to Natural Waters, Eisenreich SJ, ed., Ann Arbor Science Pubs. (in press).

Giam CS, Chan HS, Neff GS, Atlas E. 1978. Phthalate ester plasticizers: A new class of marine pollutant. Science 199:419.

Giam CS, Atlas E, Chan HS, Neff GS. 1980. Phthalate esters, PCB and DDT residues in the Gulf of Mexico atmosphere. Atmos. Environ. 14:65-69.

Gilbertson M. 1976. Background to the regulation of PCBs in Canada, Task Force on PCB. Rep. to Environmental Contaminants Committee of Environment Canada and Health and Welfare, Canada.

Grosjean D, Friedlander SK. 1975. Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere. J. Air. Pollut. Control Assoc. 25:1038.

Harvey GR, Steinhauer WG. 1974. Atmospheric transport of polychlorinated biphenyls to the North Atlantic. Atmos. Environ. 8:777.

Hollod GJ. 1979. PCBs in the Lake Superior ecosystem: Atmospheric deposition and accumulation in the bottom sediments. Dissertation, University of Minnesota, Minneapolis.

Junge CE. 1975. Transport mechanisms for pesticides in the atmosphere. Pure Appl. Chem. 42:95.

Junge CE. 1977. Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. In: Fate of Pollutants in the Air and Water Environments, Part 1. (Advances in Environmental Science and Technology, Vol. 8), Suffet IH, ed., Wiley-Interscience, New York.

Karickoff SW, Brown DS, Scott TA. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241.

Liss PS, Slater PG. 1974. Flux of gases across the air-sea interface. Nature 247:181.

MacKay D, Wolkoff AW. 1973. Rate of evaporation of low-solubility contaminants from water bodies to the atmosphere. Environ. Sci. Technol. 7:611.

MacKay D, Shiu WY, Sutherland RP. 1979. Determination of air-water Henry's Law constants for hydrophobic pollutants. Environ. Sci. Technol. 13:333.

McClure VE. 1976. Transport of heavy chlorinated hydrocarbons in the atmosphere. Environ. Sci. Technol. 10:1223.

Melnikov NN. 1971. Chemistry of Pesticides, Springer-Verlag, New York.

Mosser JL, Fisher NS, Wurster CF. 1972. Polychlorinated biphenyls and DDT alter species composition in mixed cultures of algae. Science 176:533.

Murphy TJ, Rzeszutko CP. 1977. Precipitation inputs of PCBs to Lake Michigan. J. Great Lakes Res. 3:305.

_____. 1978. PCBs in precipitation in the Lake Michigan basin. Rep. to US-EPA on Grant No. 803915, Environmental Research Laboratory, Duluth (EPA-60013-78-071).

Murphy TJ, Heeson TC, Young DR, McDermott-Ehrlich D. 1980. Evaluation of a technique for measuring dry aerial deposition rates of DDT and PCB residues. Atmos. Environ. (in press).

Nisbet ICT, Sarofim AF. 1972. Rates and routes of transport of PCBs in the environment. Environ. Health Perspect. 1:21.

Peel DA. 1975. Organochlorine residues in Antarctic snow. Nature 254:324.

Pupp C, Lao RC, Murray JJ, Pottie RF. 1974. Equilibrium vapor concentrations of some PAH, As_4O_6, and SeO_2 and the collection efficiencies of these compounds. Atmos. Environ. 8:915.

Risebrough RW, Rieche P, Peakall DB, Herman SG, Kirven NM. 1968a. PCBs in the global ecosystems. Nature 232:50.

Risebrough RW, Griffin JJ, Huggett RJ, Goldberg ED. 1968b. Pesticides: Trans-Atlantic movement in the Northeast Trades. Science 159:1233.

Simon CG, Bidleman TF. 1979. Sampling airborne PCB with polyurethane foam plugs. Anal. Chem. 51:1110.

Slinn WGN, Hasse L, Hicks BB et al. 1978. Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. Atmos. Environ. 12:2055.

Slinn SA, Slinn WGN. 1980. Modeling of atmospheric particulate deposition to natural waters. In: Atmospheric Input of Pollutants to Natural Waters, SJ Eisenreich, ed., Ann Arbor Science Pubs. (in press).

Strachan WMJ, Huneault H. 1979. Polychlorinated biphenyls and organochlorine pesticides in Great Lakes precipitation. J. Great Lakes Res. 5:61.

Van Vaeck L, vanCauwenberghe K. 1978. Cascade impactor measurements of the size distribution of the major classes of organic pollutants in atmospheric matter. Atmos. Environ. 12:2229.

Wildish DJ. 1972. Polychlorinated biphenyls (PCBs) in sea water and their effect on reproduction of Gammarus Oceanicus. Bull. Environ. Cont. Toxicology 7:182-187.

Part III

GUIDE FOR ESTIMATING DEPOSITION RATES OF GASES AND AEROSOLS

B. C. Scott (Chairman), L. A. Barrie, D. F. Gatz,
J. M. Miller and D. H. Pack

1. INTRODUCTION

The natures of depositional processes and atmospheric transport are such that, as space and time scales increase, the ability to estimate deposition rates improves. In this section, no attempt has been made to describe depositional processes that might occur over a few tens of kilometers or within a few hours. Rather the removal parameterizations are for materials relatively uniformly concentrated in the lowest several kilometers of the atmosphere and for time and space scales on the order of 1 year and 1,000 kilometers. These scales permit atmospheric variability in directional transport, storm paths, stability, etc., to be smoothed or averaged.

A guide for estimating deposition rates for gases and aerosols has been provided to be used with specific information about the physical and chemical properties of the gas or aerosol involved. Simple rules for estimating both wet- and dry-deposition rates are presented in terms of parameters called washout ratios and deposition velocities.

The following tables and formulas provide only deposition rates. The user must determine the time interval involved to compute total deposition. However, the procedure for determining relative contributions of wet and dry deposition on an annual basis is also given. Air concentrations of the material involved must also be known as well as how it is distributed, e.g., as a gas, as an aerosol, or as both (see Parts I and II).

A great deal of uncertainty can result from using the approaches outlined below. The deposition rates obtained from the simplified tables and formulas should be considered accurate only to within a factor of 2 or 3 of the true values. More accurate estimates would require extensive investments of time and money. If applications of the procedures presented here suggest that particular materials are potentially damaging, then more accurate procedures or even laboratory or field experiments should be used to refine those estimates. Indeed, one part has been devoted to considerations that must be recognized when computing deposition where the well mixed, annually averaged atmosphere is clearly not appropriate. There are also references for complex models and for publications with additional details on deposition calculations.

Finally, implementation of the research recommendations as listed at the end of this section is mandatory to the advancement of the existing knowledge on estimating the deposition of pollutants.

2. WET REMOVAL AND DEPOSITION OF AEROSOLS AND GASES

2.1 Wet Removal of Aerosols

Regardless of how the wet removal of aerosols from the atmosphere is described, the concentration of the pollutant x_p associated with precipitation must first be considered. Because most aerosol pollutants associated with precipitation first attach to suspended cloud droplets, both the collection of and the chemistry of the tiny cloud droplets must be considered in deriving x_p. Aerosols not attached directly to cloud droplets can also be scavenged by falling precipitation particles.

What is being considered here is therefore a system with two rate-limiting processes (listed below). First, an aerosol attaches to the condensed water; second, the condensed water falls. The slower of the two rates determines the rate of deposition at the surface.

Rate Limiting Processes

(1) Attachment
  (a) Collection efficiency
  (b) Solubility
  (c) Size
  (d) Condensation, evaporation
  (e) Age
(2) Removal
  (a) Precipitation growth processes (riming, accretion, etc.)
  (b) Storm efficiency
  (c) Seasonal variations

2.1.1 Attachment

The collection and collision efficiencies are the most important and the most difficult attachment processes to estimate. Figure III-1 illustrates how sensitive collection is to the size of the collected and collector particles.

Particulate solubility is also important in determining the size of the aerosol. During precipitation, subcloud humidities are typically between 90% and 100%. At these humidities, initially dry, soluble aerosols will rapidly increase their dimensions by a factor of 4 or more. Figure III-2 shows the

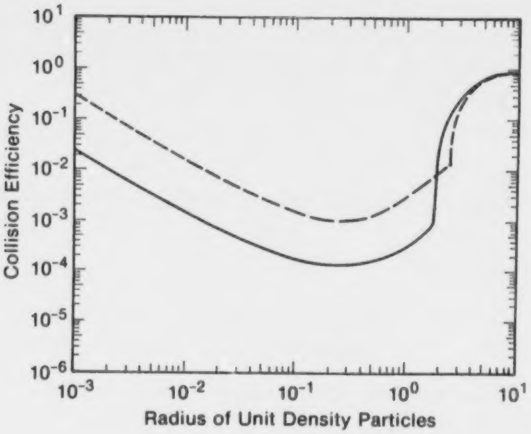


Figure III-1. Collision efficiency as a function of size of the collected particles. Radii of collector particles are 0.1 mm (dashed line) and 1.0 mm (solid line) (after Slinn 1977).

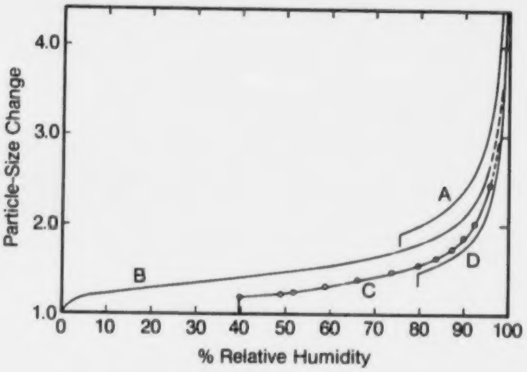


Figure III-2. Theoretical growth curves for solution droplets of sulfuric acid and some inorganic salts at 25°C (after Tang and Munkelwitz 1977). A = NaCl; B = H_2SO_4; C = NH_4HSO_4; D = $(NH_4)_2SO_4$.

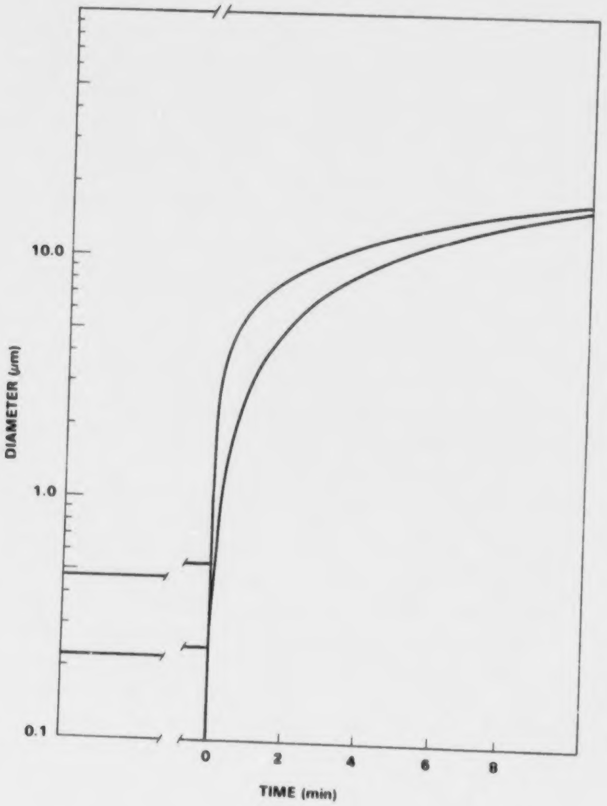


Figure III-3. Growth of aerosol composed of 50% ammonium sulfate.
S = 0.1%; $(NH_4)_2SO_4$ = 50%.

relationship between the size of various soluble materials and humidity.

How long it takes a soluble aerosol to grow to cloud-droplet size depends on what fraction of the particle is composed of soluble material and on various cloud micro-physical properties (such as, updraft velocity, temperature, and the number of aerosols competing for available water). Figure III-3 illustrates how an aerosol composed of 50% ammonium sulfate responds after being drawn into a cloud with water supersaturation of 0.1%. Under these conditions, the growth of a submicron-size aerosol to cloud-droplet size (10-μm diameter) takes 2 min or less.

Aerosol growth in the humid-cloud environment also presents a likely pathway for the removal of insoluble material from the atmosphere. Consider, for example, insoluble lead (Pb) aerosol, thought to be attached to particles with a mass median diameter (mmd) of ~0.5 μm. The tiny Pb-containing particles would ordinarily be difficult to remove (see Figure III-1) because of their size. However, if the Pb is attached to a particle that is partially soluble, then, upon entering a cloud, it would almost instantly be incorporated into the cloud water and within minutes would achieve a maximum collision efficiency of 1. This rapid growth of aerosol to cloud-droplet size is often called nucleation scavenging. Thus, the age of an aerosol is also important; the older an aerosol, the larger its mean diameter--because of coagulation--and the greater the likelihood that it will attach to a soluble aerosol.

2.1.2 Removal of Aerosol

To properly discuss removal processes, distinctions must be made between ice growth and water growth after cloud and precipitation water have formed. Ice-growth processes probably start most precipitation in our latitudes. However, during warm seasons or at high freezing levels (∿3 km), the coalescence process involving water/water collisions becomes the dominant precipitation-growth mechanism. Condensation onto drops always remains a minor factor in the growth of precipitation. Thus when coalescence is important, a 1-mm raindrop is produced from about a million collisions with cloud droplets. Rather than being diluted, as would occur if condensation were important, the concentration of a pollutant is increased or decreased depending on the amount of pollutant in the collected droplets. That a raindrop acts as a concentrating agent is clearly demonstrated by noting that one drop takes 10^6 cloud droplets with a mean spacing of ∿1 mm between droplets and places them all into a volume of about 1 mm^3, i.e., a concentration factor of 10^6. This concentrating of pollutant is the physical basis behind the washout ratio W.

The washout ratio is an empirical relationship, valid over one month or more. Expected pollutant concentrations in rain can be empirically related to known or assumed concentrations in the air at ground level on the basis of previous measurements of both quantities. When W is expressed as a volume-weighted ratio (mass of pollutant per volume of rain water divided by mass of pollutant per volume of air), the values are typically near 10^6, implying that (1) the aerosol has been readily incorporated into the cloud water, (2) the aerosol is probably soluble, and (3) precipitation is formed primarily through a coalescence process. Also implied is that the concentration of a pollutant measured in air near the ground is representative of the concentration averaged over approximately 3 km--from the ground through the cloud.

Physical interpretation of the scavenging mechanisms is difficult if the precipitation is snow or is falling from a cold cloud with low freezing levels--particularly if the washout ratio is on the order of 10^5. Although precipitation from these cold clouds may be predominantly snow, they can contain abundant quantities of supercooled liquid water (average concentrations

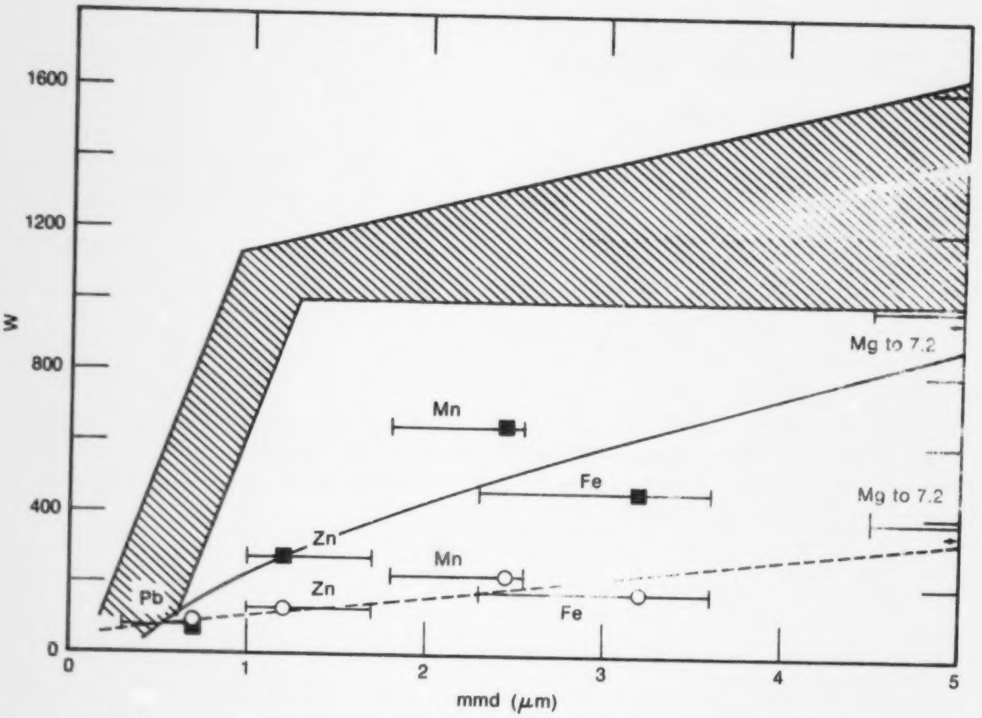


Figure III-4. Variation of the precipitation-weighted mean washout ratio W (dimensionless) with the mass median diameter (mmd). Cross-hatched area = Chilton, United Kingdom (after Cawse 1977); straight line and ■ = 50 km northwest of St. Louis, MO (after Gatz 1975); dashed line and o = 15 km northeast of St. Louis, MO (after Gatz 1975).

near $\sim$0.1 g m^{-3}). The collection of this supercooled water by snow flakes (called riming) is the dominant mechanism for removing soluble aerosols from cold clouds. However in spite of this water-mass contribution from riming, one-half or more of the precipitation mass from cold clouds usually results from vapor deposition (the ice analogy of liquid-phase condensation). In other words, in cold clouds precipitation particles grow primarily because water vapor is depositing upon their surfaces by sublimation. This direct deposition of vapor is only of minor importance in warm clouds. Thus, in cold clouds only 10^5 or fewer collisions with cloud droplets are needed to produce a 1-mm raindrop at ground level--the additional mass being obtained by vapor deposition. In a cold cloud, therefore, washout ratios for soluble aerosols should drop to 10^5 or less. Thus, a washout ratio of $\leq 10^5$ can indicate that efficient ice-phase mechanisms are operating in a cloud. Equally likely, however, is that such low washout ratios imply that an aerosol is not being efficiently attached to the cloud water. Aerosols that are insoluble or relatively young, or have dimensions between 0.1 to 1.0 μm are not easily scavenged (Figure III-4).

2.2 Wet Deposition of Aerosols

2.2.1 Air Concentrations

Before leaving the discussion of washout ratios and aerosol scavenging, it is important to show how the surface-deposition rate D is related to the washout ratio.

Surface-deposition rate D is given by

$$D = (JC)_0, \qquad (2\text{-}1)$$

where C is the pollutant concentration in precipitation (units of mass of pollutant per mass of water) and J is the precipitation rate (units of mass of water per unit area per unit of time). Washout ratio W is defined as

$$W = \frac{C}{(x_a)_0} \;, \qquad (2\text{-}2)$$

where $(x_a)_0$ is the air concentration measured at the ground. Substitution of Eq.2-2 into Eq.2-1 provides the relationship between the washout ratio and the surface-deposition rate:

$$D = W(Jx_a)_0 \; . \qquad (2\text{-}3)$$

For total deposition, Eq.2-3 is multiplied by the total units of time.

All deposition expressions assume that the subcloud-air concentration of pollutants can be determined for each precipitation event by constructing air trajectories. The construction of appropriate trajectories is too involved to be covered here. Suffice it to say, constant-level trajectories based on average winds are totally inadequate for describing source regions and travel times to a receptor during periods of precipitation. Vertical air motions, pollutant convergence, and scavenging along the path of the trajectory must all be considered when determining air concentrations at a receptor.

2.2.2 Rates of Wet-Deposition of Aerosol

To calculate wet-deposition rates, use Eq. 2-3 with the appropriate value of W from Table III-1. These values are applicable only to long-term deposition (approximately 1 yr), averaged over large regions, and at locations far enough away from local sources for the materials to have uniform concentrations with height. Separate estimates should be made for the convective and continuous portions of the precipitation and then added for total deposition.

Table III-1. Washout Ratios (volume basis)

Particle mmd (μm)	Convective rainfall	Continuous rainfall
>1	5×10^5	10^6
<1	10^5	2×10^5

The respective W values for convective and continuous precipitation reflect what is currently known about wet removal for these two classes. Within these classes, W may vary as a function of precipitation rate. Further research is needed both to verify the overall average values for each class and to gather information on how W varies with precipitation rate within each class.

These calculations will yield only a gross estimate of the deposition of a given material, accurate to within a factor of perhaps 3. If such an assessment shows even a marginal potential for harmful effects from wet or dry deposition, laboratory or field studies should measure the actual atmospheric-deposition characteristics of the substance in question.

2.3. Wet Removal of Gases

Unlike aerosol scavenging, gas scavenging is often reversible. Gases can be absorbed, desorbed, and chemically altered in condensed water. As with aerosols, however, the phases of the condensed cloud water and of the collector particles are important in determining the deposition rate at the surface.

In general, the flux of a gas into or out of a single raindrop can be related to the diffusivity of the gas D and to the gradient of gas concentration C near the drop of radius r_o:

$$\text{Flux} = D \frac{\partial C}{\partial r_o} \quad . \tag{2-4}$$

The change of pollutant mass within a drop of radius r_o is then given by

$$V_t \frac{d}{dz}\left(C \frac{4}{3} \pi r_o^{\ 3}\right) = 4\pi r_o D (C_{eq} - C)(1+F), \tag{2-5}$$

where V_t is the fall speed of a drop, C_{eq} the equilibrium concentration of a gas in water at an air concentration of x_a, and C the actual concentration of a gas in water. The term (1+F) is a semi-empirical correction for the ventilation of a drop as it falls through the environment. From Eq.2-5, an e-fold equilibrium distance can be computed (i.e., the fall distance Z required to reach ~63% of the equilibrium value):

$$Z \sim \frac{r_o^2 V_t}{3D(1+F)} \quad . \tag{2-6}$$

Thus, we see that the bigger the drop and the smaller the diffusivity, the longer it takes for a drop to come into equilibrium with the environment. However, using reasonable values for the parameters in Eq.2-6 establishes

$$Z < 1 \text{ m} \; . \tag{2-7}$$

The equilibrium time t is

$$t < 1 \text{ s}. \tag{2-8}$$

Therefore, the gas concentration in liquid water should be very close to the equilibrium value determined by the gas concentration in the environment; i.e.,

$$C \sim C_{eq}$$

where

$$C_{eq} = \frac{x_a}{H} \tag{2-9}$$

and H is the Henry's law constant.

For liquid precipitation, this equilibrium concentration is strongly controlled by surface-air concentrations. For snow, however, this equilibrium concentration is determined at the altitude of impact between supercooled cloud droplets and collecting snowflakes. The collisions rapidly freeze the cloud droplets and prevent any readjustment to near-equilibrium values at lower altitudes.

Thus to determine correct wet removal rates by snow, the air concentrations of pollutants within a cloud must be estimated. Unfortunately this cloud-level concentration is rarely known, and the best one can do is to use surface-level concentrations in the removal calculations.

2.4 Wet Deposition of Gases

Recalling the definition of the washout ratio (Eq.2-2), for gases we have

$$W = \frac{1}{H} \ . \tag{2-10}$$

The surface deposition rate (see Eq. 2-3) is then given by

$$D = \frac{Jx_a}{H} \ . \tag{2-11}$$

The values used for the solubility expression H must be appropriate for typical atmospheric conditions. That is, H must be evaluated at temperatures between 0° and 25°C, at different air concentrations x_a, and at different ionic concentrations in rainwater (e.g., pH).

To compute the deposition rate of gases, a washout ratio is not needed; as noted in Eq.2-11, knowing the Henry's law constant is sufficient. Therefore, as a first approximation, wet removal of gas is independent of season and location and depends only upon the Henry's law constant.

Groups of materials, e.g., PCBs, DDT, etc., that have similar values of H should be identified. A single value of H could then be used for certain classes of molecules, thereby eliminating the need for tests for every material within a class.

Eq.2-11 must be used with caution. Various gases thought to be harmless or proven to be inefficiently removed by different depositional processes may combine with or transform to materials (gases or aerosols) with entirely different properties. Research concerning the transformation products of every new gas is mandatory.

Surfaces do not necessarily retain gases deposited on them. For example, many pesticides and PCBs evaporate from the ground quite readily (Junge 1977, Spenser and Cliath 1969) and Hg can be reemitted at locations of previous deposition (Hogstrom et al. 1979). In addition, the drying of a wet surface can result in reemission caused by increased concentrations in the aqueous phase.

3. DRY REMOVAL AND DEPOSITION OF AEROSOLS AND GASES

Particles and gases are removed from the atmosphere not only by precipitation but also by direct uptake at the earth's surface. The rate at which this occurs is governed by several processes acting simultaneously. Each process has a transfer resistance associated with

(1) Turbulent transport through the atmospheric boundary layer r_a;
(2) Inertial penetration and molecular diffusion through the near-surface air layer r_b;
(3) Uptake at the surface r_s.

The total transfer resistance is then

$$r = r_a + r_b + r_s \quad . \tag{3-1}$$

The inverse of r is the deposition velocity V_d used to calculate deposition flux F:

$$F = V_d C \ , \tag{3-2}$$

where C is the pollutant's atmospheric concentration at 1-10 m above this surface. When dry removal is computed, C and V_d can be considered independent of height above 1 m from the surface.

The relative importance of atmospheric transport (r_a+r_b) and surface capture (r_s) is primarily governed by the level of turbulent mixing in the boundary layer and the reactivity of the pollutant with the surface. If surface resistance to pollutant transfer is high, as for chlorofluoromethanes, then the surface processes become rate limiting. On the other hand, if a surface is a perfect sink for a pollutant (viz., uptake of SO_2 by the Great Lakes), then the atmospheric-transport processes are rate limiting. Many pollutant/surface combinations fall between these two extremes and, therefore, both atmospheric and surface resistance to transfer must be taken into account.

3.1 Dry Removal of Aerosols

Most particulates in the atmosphere have a diameter of 0.01-10 μm. Because of the dynamics of particle production, growth, and interaction, these size ranges are not uniformly distributed but rather are concentrated in modes (Whitby 1978): a nucleus mode, centered on particle diameters of 0.05 μm; an accumulation mode, centered on particle diameters of 0.4 μm; and a coarse-particle mode, centered on particle diameters of 5 μm. The nucleus mode is maintained by a dynamic equilibrium between particle production by condensation processes and particle removal by adsorption onto the surfaces of accumulation-mode aerosols. If production is stopped, particles in the nucleus mode expand to the accumulation mode by coagulation within a few hours. Particles in the accumulation mode are created from nucleus-mode particles and primary emissions. The coarse-particle mode comprises wind-blown-dust particles and coarse particles from primary emissions, such as flyash. Most suspended particulates in the atmosphere are in the accumulation or coarse-particle modes.

3.2 Dry Deposition of Aerosols

Particles are deposited onto surfaces by various processes. Particles with diameters smaller than 0.3 μm are deposited by Brownian diffusion, those with diameters ranging from 0.3 to 5 μm by inertial impaction-interception, and those with diameters greater than 5 μm by gravitational sedimentation. Because Brownian diffusion increases as particle size decreases below 0.3 μm and inertial interception-impaction increases as particle size increases above 0.5 μm, there is a minimum in the deposition velocity in the size range of 0.3-0.5 μm. The relationship between deposition velocity and particle size resembles that for particle-collection efficiency by raindrops (Figure III-1).

In Table III-2 particle-deposition velocities to land and water surfaces are given for two ranges of particle size. These are only order-of-magnitude estimates for dry-deposition removal. The V_d values are uncertain by about a factor of 3. Should a substance be of serious environmental concern, more detailed investigations should be undertaken. Such studies must first establish the substance's particle-size distribution in the atmosphere and then measure actual deposition velocities to the receptor surfaces under field conditions.

Table III-2. Particle-Deposition Velocities (cm s^{-1})

	Land	Water
Coarse-particle mode (1 μm < D < 10 μm)	1	1
Accumulation mode (0.1 μm < D < 1 μm)	0.2	1

NOTE: D is the mass median diameter; particle size refers to aerodynamic size.

3.3 Dry Deposition of Gases

The quantitative prediction of the dry-deposition velocity of a gas to the earth's surface is complicated by the multitude of surfaces involved (see Garland 1978). Since this assessment was not meant for such detailed work, a first approach to making an order-of-magnitude estimate of deposition velocity is outlined below. Should the gas involved be of environmental concern, more detailed studies must be done under actual field conditions.

As mentioned before, the dry-deposition rate of gases is dependent on the resistance to atmospheric transport and on the resistance to uptake at the surface. For most environmental surfaces, the surface resistance to SO_2-uptake is of the same order of magnitude as the atmospheric-transport resistance; consequently SO_2 deposition rates are controlled by both atmospheric and surface processes. However, if a gas is 10 times less reactive with a surface than SO_2 is, its deposition is mainly limited by surface uptake. By making a simple laboratory comparison of the relative reaction of a gas and sulfur dioxide with an environmental surface, an estimate can be made of that gaseous deposition velocity. Therefore, the following procedure is recommended.

Through a laboratory study, determine the Jekyll number J_k defined as

$$J_k = \frac{(r_s)_{\text{substance } x}}{(r_s)_{SO_2}} \quad . \tag{3-3}$$

The Jekyll number is the surface resistance of the substance relative to that of sulfur dioxide. Experimentally it is the ratio of the half-life decay time, $T_{1/2}$, of each substance in a well-mixed chamber containing the natural surface of interest in a condition similar to that found in nature (see Payrissat and Beilke 1975). Actual conditions must be simulated. For instance, if the uptake of chlorofluoromethanes by sand is being tested, sunlight should be present. Wall losses in the chamber must always be taken into account.

If J_k is 10 or greater, the atmospheric dry-deposition process is controlled by the surface uptake. Surface uptake rates are actually measured in the chamber experiment and the V_d in cm s^{-1} is given by

$$V_d = \frac{(100\ h)\ln 2}{T_{1/2}} \tag{3-4}$$

where h is the height of the test chamber in meters and $T_{1/2}$ is the half-life of the gaseous substance of interest in seconds in a 1-m^2 chamber of height h whose bottom is covered with the natural surface of interest and in which air is well mixed by fans.

If J_k is less than 10, the dry-deposition process is controlled not only by surface uptake but also by transport through the atmospheric boundary layer. The latter is governed by the time of year and the surface type. Ranges expected for the V_d in these circumstances are listed in Table III-3.

Table III-3. Ranges of V_d for a Substance with a Jekyll Number < 10 (cm s^{-1})

Surface Type	Season	
	Summer	Winter
Land	0.5-2	0.05-0.2
Water	0.05-0.2	0.5-2

These kinds of calculations give only gross estimates of the deposition of a given material, accurate to within a factor of perhaps 3. If such an assessment shows even a marginal potential for harmful effects from wet or dry deposition, laboratory or field studies should measure the actual atmospheric-deposition characteristics of the substance in question.

4. RELATIVE REMOVAL BY WET AND DRY PROCESSES

To estimate the relative removal by wet and dry deposition, the dry flux of a material is approximated as

$$F_d = V_d x_a \tag{4-1}$$

and the wet flux as

$$F_w = W x_a J \ . \tag{4-2}$$

Dry flux can occur throughout the year (denoted as Δt) but wet flux occurs only during periods of precipitation (denoted as Δt_w). The ratio R of wet to dry deposition is given by

$$R = \frac{J \Delta t_w W}{V_d \Delta t} \ . \tag{4-3}$$

Here, the product $J\Delta t_w$ is the annual precipitation amount A. Therefore,

$$R = \frac{AW}{V_d \Delta t} \ . \tag{4-4}$$

For example, for a deposition velocity of 0.2 cm s^{-1}, a washout ratio of 2×10^5 and an annual precipitation amount ($\Delta t = 3.15 \times 10^7$ s) of 90 cm, the ratio of wet to dry deposition would be about 3. This value of 3 implies that 75% of the total deposition is due to wet removal.

5. SPECIAL SITUATIONS

The averagings given in this section may not be applicable for

(1) Unique emission configurations--those that do not produce (relatively) uniform atmospheric concentrations;
(2) Unique receptor configurations--primarily single locations for which deposition values are required;
(3) Unique meteorological environments
    (a) Coastal areas with frequent sea/land breezes;
    (b) Arctic environments with persistent low-level stability (i.e., surface inversions) and snow cover;
    (c) Precipitation extremes: arid or wet.

Other methodologies can be applied to estimate the deposition for these situations.

5.1 Unique Emission Configurations

If the emissions of a compound exceed about 10% of the area or national total for that compound and if the source of emission is relatively isolated from other significant releases (500-1000 km away), atmospheric transport and dilution should be carefully analysed.

The above value of 10% for a single source is based on an analogy with sulfur emissions. Here a single site in Sudbury, Ontario, is the source of approximately 10% of the total sulfur emitted in North America. This emission rate is detectable several hundreds of kilometers from the stack.

The techniques for a detailed approach are well known (Turner 1970, Pasquill 1974, 1978, Haugen 1975). For short periods of up to about one month, observations of wind direction, wind speed, and stability can be used to calculate the distribution of a three-dimensional plume concentration. Dry deposition can then be calculated by applying the appropriate deposition velocity (V_d as previously defined) with the necessary corrections for the removal of a material from a plume (e.g., Horst 1977, Hogstrom 1979).

Wet deposition is best estimated from observed precipitation amounts and types (Hales 1972, 1975). The techniques are reasonably accurate for the distance a plume travels in 10-20 h (~200-

500 km). Beyond these distances, vertical concentration becomes uniform and the methods described previously for dry deposition can be applied along the path the material travels.

On the other hand, wet removal of a material from a discrete source at long distances is much less certain since precipitation indicates significant vertical motion. These vertical motions carry material aloft into layers moving in different directions and at different speeds. They further permit the incorporation of compounds into clouds with the subsequent possibility for aqueous chemistry modification. Studies of storm characteristics (e.g., Kreitzberg and Leach 1979) indicate the rapid incorporation of surface air into higher levels of storm systems, sometimes from a location 180° opposite to that of the surface airflow.

There are few validated wet-deposition data for these situations. However, Smith and Hunt (1978) have shown that individual storms produce large amounts of wet deposition even from area sources. Also nuclear-test debris has been removed by rain thousands of kilometers from its source, further supporting both the significance of the process and its explicit relation to individual storms.

Accurate quantitative evaluation of this phenomenon will require research on the mesoscale flow patterns of precipitation systems combined with measured data on vertical concentration profiles and concentrations in collected precipitation (e.g., Gatz 1980).

5.2 Unique Receptor Configurations

These are usually individual locations where deposition levels are required, e.g., a lake, an urban complex, an agricultural or forest plot.

As a general approach, site-specific data should be used to calculate removal. For uniformly distributed material, the methodology suggested for the regional approach can be modified to use actual precipitation data (frequency, amounts, and rainfall rates) for wet deposition. For dry deposition, the actual or estimated atmospheric concentrations should be used in conjunction with deposition velocities that reflect the specific roughness characteristics of the actual locations, which can vary with the season. For example, dry deposition on an open-water surface will differ from that on a frozen lake; grassland deposition will differ from that on a snow-covered surface; and removal by forests in leaf will differ from removal during bare-branched winter conditions.

Unfortunately few data on dry-deposition velocity exist for all these situations, even for the conventional pollutants. For new compounds, surrogate data should be used, i.e., data based on similarity of forms (gaseous or particulate), size distributions, and surface reactivities (see Section 3). At the time of this publication, the single most comprehensive collection of V_d data is that tabulated by McMahon and Denison (1979), and studies of this phenomenon are continuing (e.g., Barrie and Walmsley 1978).

If removal calculations must be carried out for a compound that is not well mixed but that originates from a significant source within, say 500 km, "back-track" meteorological trajectories (e.g., Heffter et al. 1975) separated into precipitation/non-precipitation occurrences will give more relevant statistics.

5.3 Unique Meteorological Environments

5.3.1 Coastal Areas

These situations will be important, primarily, to discrete sources or discrete receptor calculations of deposition. For example, for a location with a daily onshore sea breeze (non-source flow) and nocturnal land breeze (potential source flow--the sea), deposition calculations would be relevant only for the flow from the source, i.e., at night.

Not all special circumstances can be covered here. Coastal, mountainous, and ocean environments should be carefully considered before applying any generalized methods.

5.3.2 Precipitation Extremes

Two additional environmental circumstances--very arid or desert areas and very rainy areas--should also be treated as special cases. If the area has only infrequent and sparse precipitation, first calculate the ratio of wet to dry deposition, R:

$$R = \frac{AW}{V_d \Delta t} . \qquad (5\text{-}1)$$

For annual precipitation amounts typical of deserts, dry deposition probably predominates. For example, an annual rainfall of only 12.7 cm would remove about 30% of the small particulates. Attention could then be focused on details of the dry-removal processes.

Alternatively, a detailed examination of a storm using actual observations of individual precipitation events--rainfall rates, storm type, etc.--would improve the estimates.

The converse would be true for locations with copious precipitation. Annual precipitation values near 508 cm yr^{-1} (e.g., in portions of southeast Alaska) could remove more than

90% of the fine particulates. Under such circumstances, dry deposition would be unimportant.

Not all the special circumstances where generalized methods could be applied are covered here. Each new compound, its source distribution, physical/chemical character, and potential for environmental effects must be considered in deciding what methods to use.

6. RESEARCH RECOMMENDATIONS

The research recommended below is mandatory if the uncertainty inherent in deposition calculations is to be alleviated:

(1) Washout ratios for aerosols must be classified by storm type, location, season, rainfall rate, size, and mass median diameter over many locations and seasons. The size distribution and the mass median diameter of each aerosol must also be reported.

(2) Gases must be grouped by their chemical and physical properties to determine if such categorization relates to the deposition properties.

(3) How much gas is reemitted to the atmosphere must be determined. Many gases are transported to the surface but may be reemitted to the atmosphere after deposition on the ground.

(4) Extensive measurements of the deposition velocity to various surfaces (especially forests) are necessary to define the dry deposition of aerosols more precisely. Snow and ice fields, water surfaces, forests, grasslands, and other surfaces influence how much aerosol is captured.

(5) Use of the Jekyll number should be developed and refined. The dry deposition of a chemical is a difficult parameter to determine. A known gas such as SO_2 can be compared with an unknown gas to define the Jekyll number. This practical method could be used to standardize procedures for evaluating how important the dry deposition of a given gas is to total deposition.

7. REFERENCES

Barrie LA, Walmsley JL. 1978. A study of sulfur dioxide deposition velocities to snow in Northern Canada. Atmos. Environ. 12:2321.

Cawse PA. 1974. A survey of atmospheric trace elements in the United Kingdom. AERE Rep. R7669, Harwell.

Garland JA. 1978. Dry and wet removal of sulfur from the atmosphere. Atmos. Environ. 12:349.

Gatz DF. 1975. Scavenging ratio measurements in METROMEX. ERDA Symposium on Precipitation Scavenging 1974-Coordinators RW Beadle, RG Semoin, NTIS-74-1014, pp. 71-87.

Gatz DF. 1980. Association and mesoscale spatial relationships among rain water constituents. J. Geophys. Res. (in press).

Hales JM. 1972. Fundamentals of the theory of gas scavenging by rain. Atmos. Environ. 6:635.

_____. 1975. Atmospheric transformations of pollutants. In: Lectures on Air Pollution and Environmental Impact Analyses, DA Haugen, ed., American Meteorological Society, Boston, MA.

Haugen DA, ed. 1975. Lectures on Air Pollution and Environmental Impact Analyses. American Meteorological Society, Boston, MA.

Heffter JL, Ferber GJ, Taylor AD. 1975. A regional-continental scale transport, diffusion, and deposition model. NOAA Tech. Mem., ERL-ARL-50. Air Resources Laboratories, Silver Spring, MD.

Hogstrom U. 1979. Initial dry deposition and type of source in relation to long distance transport of air pollutants. Atmos. Environ. 13:295.

Hogstrom U, Enger L, Svedung I. 1979. A study of atmospheric mercury dispersion. Atmos. Environ. 13:465.

Horst TW. 1977. A surface depletion model for deposition from a Gaussian plume. Atmos. Environ. 11:41.

Houze RH Jr., Locatelli JD, Hobbs PV. 1976. Dynamics and cloud microphysics of rainbands in an occluded frontal system. J. Atmos. Sci. 33:1921.

Junge CE. 1977. Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. In: Fate of Pollutants in the Air and Water Environment (Advancement in Environmental Sciences and Technology series), Suffet IH, ed., Wiley-Interscience, New York.

Kreitzberg CW, Leach MJ. 1979. Diagnosis and prediction of tropospheric projectories and cleansing. In: Proceedings of Advisory Workshop to Identify Research Needs on the Formation of Acid Precipitation, Electric Power Research Institute, Palo Alto, CA.

McMahon TA, Denison PJ. 1979. Empirical atmospheric deposition parameters--a survey. Atmos. Environ. 13:571.

Pasquill F. 1974. Atmospheric Dispersion. Halstead Press, New York.

_____. 1978. Atmospheric dispersion parameters in plume modelling. EPA Rep. EPA-600 4-78-021.

Payrissat M, Beilke S. 1975. Laboratory measurements of the uptake of sulfur dioxide by European soils. Atmos. Environ. 9:211.

Slinn WGN. 1977. Some approximations for the wet and dry removal of particles and gases from the atmosphere. Water Air Soil Poll. 7:513.

Smith FB, Hunt RD. 1978. Meteorological aspects of the transport of pollution over long distances. Atmos. Environ. 12:461.

Spencer WF, Cliath MM. 1969. Vapor density of dieldrin. Environ. Sci. Technol. 31:670.

Tang IN, Munkelwitz HR. 1977. Aerosol growth studies: III. Ammonia bisulfate aerosols in a moist atmosphere. J. Aerosol Sci. 8:321.

Turner DB. 1970. Workbook of Atmospheric Dispersion Estimates. EPA, Research Triangle Park, NC.

Whitby KT. 1978. Physical characteristics of sulfur aerosols. Atmos. Environ. 12:135.

BIBLIOGRAPHY

This section contains additional references on metal and organic compounds in atmospheric deposition that the reader may find useful.

Abbott DC, Harrison RB, Tatton JO'G, Thompson G. 1965. Organochlorine pesticides in the atmosphere. Nature 208:1317.

Abdoh Y, Aghdaie N, Darvich MR, Khorgami MH. 1972. Detection of some PAH's and determination of benzo(a)pyrene in Teheran atmosphere. Atmos. Environ. 6:949.

Ahling B, Jensen S. 1970. Revised liquid-liquid partition in determination of PCBs and chlorinated pesticides in water. Anal. Chem. 42:1483.

Altshuller AP, Lonneman WA, Sutterfield FD, Kopezynski ST. 1971. Hydrocarbon composition of the atmosphere of the Los Angeles basin, 1967. Environ. Sci. Technol. 5:1009.

Andreae MO. 1980. Arsenic in rain and the atmosphere mass balance of arsenic. J. Geophys. Res. (in press).

Andren AW. 1973. In: Ecology and Analysis of Trace Contaminants, Fulkerson W, Schultz WD, Van Hook RI, eds., NSF-RANN Rep. ORNL/NSF/EATC-6, Oak Ridge National Laboratory, TN.

Antommaria P, Coon M, Demaio L. 1965. Airborne particulates in Pittsburgh associated with p,p' DDT. Science 150:1476.

Appel ER, Hoffer EM, Kothney EL, Wall SM, Haik M. 1979. Analysis of carbonaceous material in southern California atmospheric aerosols. Environ. Sci. Technol. 13:98.

Arthur RD, Cain JD, Barrentine BF. 1976. Atmospheric levels of pesticides in the Mississippi Delta. Bull. Environ. Contam. Toxicol. 15:129.

__________. 1977. DDT residues in air in the Mississippi Delta. 1975. Pestic. Monit. J. 10:168.

Atkins PR. 1969. Lead particulate matter in the environment. Paper presented at Air Pollution Control Association 62nd Annual Meeting, New York.

Baldwin MK, Bennett D, Begnon KI. 1977. The concentrations of aldrin and dieldrin and their photoisomers in the atmosphere. Pestic. Sci. 8:431.

Belot Y, Diop B, Marini T. 1971. Composition minerale de la matière particulaire en suspension dans l'air dans des zones urbaines. In: La Radioecologie Appliquée à la Protection de l'Homme et de son Environment, International Symposium of the European Community, Rome.

Bengtson S-A, Sodergren A. 1974. DDT and PCB residues in airborne fallout and animals in Iceland. Ambio 3:84.

Bertsch W, Chang RC, Zlatkis A. 1974. The determination of organic volatiles in air. J. Chrom. Sci. 12:175.

Bevenue A, Ogata JW, Hylin JW. 1972. Organochlorine pesticides in rainwater, Oahu, Hawaii 1971-1972. Bull. Environ. Contam. Toxicol. 8:238.

Bidleman TF, Olney CE. 1975. Long-range transport of toxaphene insecticide in the atmosphere of the western North Atlantic. Nature 257:475.

Bjorseth A, Lunde G, Lindskog A. 1979. Long range transport of PAHs. Atmos. Environ. 13:45.

Brar SS, Nelson DM, Kline JR, Gustafson PF, Kanabrocki EL, Moore CE, Hattori DM. 1970. Instrumental analysis for trace elements present in Chicago area surface air. J. Geophys. Res. 75:2939.

Bruland KW, Bertine K, Liode M, Goldberg ED. 1974. History of metal pollution in southern California coastal zone. Environ. Sci. Technol. 8:425.

Bunn WW, Deane ER, Klein DW, Kloepfer RD. 1975. Sampling and characterization of air for organic compounds. Water Air and Soil Poll. 4:367.

Burghardt E, Jeltes R. 1975. Gas chromatographic determination of aromatic hydrocarbons in air using a semi-automatic preconcentration method. Atmos. Environ. 9:935.

Butler LD, Burke MF. 1976. Chromatographic characterization of porous polymers for use of adsorbants in sampling columns. J. Chrom. Sci. 14:117.

Cambray RS, Jeffries DR, Topping G. 1975. An Estimate of the Input of Atmospheric Trace Elements into the North Sea and the Clyde Sea (1972-73). AERE Harwell Rep. R-7733, Her Majesty's Stationery Office, London.

Chow TJ, Bruland KW, Bertine K, Soutar A, Koide M, Goldberg ED. 1973. Lead and pollution: records in southern California coastal sediments. Science 181:551.

Cohen JM, Pinkerton C. 1966. Widespread translocation of pesticides by air transport and rainout. In: Organic Pesticides in the Environment, Gould RL, ed., American Chemical Society, Washington, DC.

Cohen Y, Cocchio W, MacKay D. 1978. Laboratory study of liquid-phase controlled volatilization rates in presence of wind waves. Environ. Sci. Technol. 12:553.

Colucci JM, Begeman CR. 1971. Carcinogenic air pollutants in relation to automotive traffic in New York. Environ. Sci. Technol. 5:145.

Commins BT, Hampton L. 1976. Changing patterns in concentrations of polycyclic aromatic hydrocarbons in the air of central London. Atmos. Environ. 10:561.

Comerford NB, White EH. 1976. Nutrient input by precipitation in north Minnesota forest ecosystem. J. Minn. Academy Sci. 42:22.

Crozat G, Domergue JL, Bogui V, Fontan J. 1973. Etude de l'aerosol atmospherique en Côte d'Ivoire et dans le Gofe de Guinée. Atmos. Environ. 7:1103.

Daisey JM, Leyko MA. 1979. Thin-layer GC method for the determination of PAH and oliphatic hydrocarbons in airborne particulate matter. Anal. Chem. 51:24.

Dams R, Robbins JA, Rahn KA, Winchester JW. 1971. Quantitative relationships among trace elements over industrialized northwest Indiana. In: Nuclear Techniques in Environmental Pollution, International Atomic Energy Agency, Vienna.

Davis AR. 1980. The Canadian Network for Sampling Organic Compounds in Precipitation. Inland Waters Directorate, Ottawa.

DeBortoli M, Pecchio E. 1976. Measurements of some halogenated compounds in air over Europe. Atmos. Environ. 10:921.

Delfino JJ. 1979. Toxic substances in the Great Lakes. Environ. Sci. Technol. 13:1462.

DeWiest F. 1978. Any factors influencing the dispersion and transport of heavy hydrocarbons associated with airborne particles. Atmos. Environ. 12:1705.

Dong L, Locke DC, Ferrand E. 1976. HPLC method for routine analysis of major parent PAH in particulates. Anal. Chem. 48:368.

Duce RA, Zoller WH, Moyers JL. 1973. Particulate and gaseous halogens in the Antarctic atmosphere. J. Geophys. Res. 78:7802.

Dudey ND, Ross LE, Noshkin VE. 1969. Application of activation analysis and GE(Li) detection techniques for the determination of stable elements in marine aerosols. In: Modern Trends in Activation Analysis, DeVoe JR, Lefleur PD, eds., Nat. Bureau of Std., Special Pub. 312, Vol. I, Washington, DC.

Egorov VV, Zhigalovskaya TN, Malakhov SG. 1970. Microelement content of surface air above the continent and the ocean. J. Geophys. Res. 75:3650.

Eichmann R, Nevling P, Ketseridis G, Hahn J, Jaenicke R, Junge C. 1979. N-alkane studies in the troposphere: I. Gas and particulate concentrations in the North Atlantic air. Atmos. Environ. 13:587.

Eisenreich SJ, ed. 1980. Atmospheric Input of Pollutants to Natural Waters, Proceedings of American Chemical Society Symposium on Metal Deposition of Lakes, Sept. 1979, Ann Arbor Science Pubs. (in press).

Eisenreich SJ, Emmling PJ, Beeton AM. 1977. Atmospheric loading of phosphorus and other chemicals to Lake Michigan. J. Great Lakes Res. 3:291.

Eisenreich SJ, Hollod GJ, Johnson TC. 1979. Accumulation of PCBs in surficial Lake Superior sediments: atmospheric deposition. Environ. Sci. Technol. 13:569.

Environmental Protection Agency. 1976. National Interim Primary Drinking Water Regulations. EPA-570/9-76-003.

Erickson MD, Michael LC, Zweidinger RA, Pellizzai ED. 1978. Development of methods for sampling and analysis of polychlorinaphthalenes in ambient air. Environ. Sci. Technol. 12:927.

Evered, DF. 1974. Decline of PCB concentrations in North Atlantic surface waters. Nature 252:387.

Faoro RB. 1975. Trends in concentrations of benzene soluble suspended particulate fraction and benzo(a)pyrene. J. Air Pollut. Control Assoc. 25:638.

Farwell SO, Robinson E, Powell WJ, Adams DF. 1976. Survey of airborne 2,4-D in south-central Washington. J. Air Pollut. Control Assoc. 26:224.

Fine DH, Rounbehler DB, Sawicki E, Krost K. 1977. Determination of dimethylnitrosamine in air, water, and soil by thermal activation analysis. Environ. Sci. Technol. 11:581.

Foster JF, Beatty GH, Howes JE, Jr. 1974. Interlaboratory Cooperative Study of the Precision and Accuracy of the Measurement of Lead in the Atmosphere using the Colorimetric Dithizone Procedure. American Society for Testing and Materials Data Series Publication DS55-S5, Battelle Memorial Institute, Richland, WA.

Fox MA, Staley SW. 1976. Determination of PAH in atmospheric particulate matter by HPLC coupled with fluorescence techniques. Anal. Chem. 48:992.

Frankel LS, Black RF. 1976. Automatic GC monitor for determination of ppb levels of bis(chloromethyl)ether. Anal. Chem. 48:732.

Fraser PJB, Pearman GI. 1978. Atmospheric halocarbons in the Southern Hemisphere. Atmos. Environ. 12:839.

Giam CS, Chan HS, Neff GS. 1975. Rapid and inexpensive method to determine PCB and phthalates in air. Anal. Chem. 47:2319.

__________. 1976. Concentration and fluxes of phthalates, DDT and PCBs to the Gulf of Mexico. In: Marine Pollutant Transfer, Windom H, Duce RA, eds., Lexington Books, Lexington, MA.

Giam CS, Chan HS, Neff GS, Atlas EL. 1978. Phthalate esters plasticizers: a new class of marine pollutant. Science 199:419.

Gordon RJ. 1976. Distribution of PAH in Los Angeles. Environ. Sci. Technol. 10:370.

Gordon RJ, Bryan RJ. 1973. Patterns in airborne PAH concentrations at four Los Angeles sites. Environ. Sci. Technol. 7:1050.

Gray D, Kay DM, Eichor J, Bogt JR. 1972. Determination of the trace element levels in atmospheric pollutants by instrumental neutron activation analysis. IEEE Trans. Nucl. Sci. NS19.

Grimsrud EP, Rasmussen RA. 1975. The analysis of chlorofluorocarbons in the troposphere by gas chromatography-mass spectrometry. Atmos. Environ. 9:1010.

Grosjean D, vanCauwenberghe K, Schmidt JP, Kelley JM. 1978. Identification of C_3-C_{10} aliphatic dicarboxylic acids in airborne particulate matter. Environ. Sci. Technol. 12:313.

Haque R, Schmedding DW. 1975. A method of measuring the water solubility of hydrophobic chemicals: Solubility of five PCBs. Bull. Environ. Contam. Toxicol. 14:13.

Hammerle RH, Pierson WR. 1975. Sources and elemental composition of aerosol in Pasadena, California by energy-dispersive X-ray fluorescence. Environ. Sci. Technol. 9:1058.

Hamilton WL, Miller JE. 1971. High lead concentrations in Columbus snow. Ohio J. Sci. 7:313.

Harding LW, Philips JH, 1978. PCBs: Transfer from microparticulates to marine phytoplankton and effects on photosynthesis. Science 202:1189.

Harrison PR, Rahn KA, Dams R, Robbins JA, Robbins JW, Winchester JW, Brar SS, Nelson DM. 1971. Areawide trace metal concentrations measured by multielement neutron activation analysis. J. Air Pollut. Control Assoc. 21:563.

Harvey GR, Steinhauer WG, Teal JM. 1973. Polychlorobiphenyls in North Atlantic ocean water. Science 180:643.

Hasan O, Spyrou NM. 1972. Air-pollution study of Guildford, Surrey, using neutron activation analysis. In: Nuclear Activation Techniques in the Life Sciences, International Atomic Energy Agency Symposium, Vienna.

Heesen TC, Young DR, McDermott ED. 1979. Evaluation of a technique for measuring dry aerial deposition rates of DDT and PCB residues. Atmos. Environ. 13:1677.

Heindryckx R, Dams R. 1974. Continental, marine, and anthropogenic contributions to the inorganic composition of the aerosol of an industrial zone. J. Radioanal. Chem. 19:339.

Henry WM, Blosser ER. 1971. Identification and estimation of ions, molecules, and compounds in particulate matter collected from ambient air. Technical Report CPA-70-159, Battelle Laboratories, Columbus, WA.

Hester NE, Meyer RA. 1979. A sensitive technique for measurement of benzene and alkyl benzene in air. Atmos. Environ. 13:107.

Hidym GM, Mueller PK, Wang HH, Karney J, Twiss S, Imada M, Alcocer A. 1974. Observations of aerosols over southern California coastal waters. J. Appl. Meteorol. 13:96.

Hoffman GL, Duce RA, Hoffman EJ. 1972. Trace metals in the Hawaiian marine atmosphere. J. Geophys. Res. 77:5322.

Hoffman GL, Duce RA, Zoller WH. 1969. Vanadium, copper and aluminum in the lower atmosphere between California and Hawaii. Environ. Sci. Technol. 3:1207.

Huntzinger O, Safe S, Zitko U. 1974. The Chemistry of PCBs, CRC Press, New York.

Ichikuni M. 1978. Calcite as a source of excess calcium in rainwater. J. Geophys. Res. 83:6249.

Jackson JW, Chang DPY. 1977. PCB recovery efficiency from stack gas and ambient air. J. Air. Pollut. Control Assoc. 27:1006.

Janssens MJ, Dams R. 1972. Analyse en interpretatie van de anorganische samenstelling der aerosolen in mechelen. Rep. of the Institute of Nuclear Sciences, University of Ghent, Belgium.

John W, Kaifer R, Rahn K, Wesolowski JJ. 1973. Trace element concentration in aerosols from the San Francisco Bay area. Atmos. Environ. 7:107.

Johnson ER, Yu TC, Montgomery ML. 1977. Trapping and analysis of atmospheric 2,4-D residues. Bull. Environ. Contam. Toxicol. 17:369.

Jones PW, Glammer RD, Strup PE, Stanford TB. 1976. Efficient collection of polycyclic organics from effluents. Environ. Sci. Technol. 10:806.

Junge CE. 1974. Residence time and variability of tropospheric trace gases. Tellus 26:477.

Katz J, Sakuma T, Ho A. 1978. Chromatographic and spectral analysis of PAH. Environ. Sci. Technol. 12:909.

Keane JR, Fisher EMR. 1968. Analysis of trace elements in airborne particulates by neutron activation and gamma-ray spectrometry. Atmos. Environ. 2:601.

Keith LH, Telliard WA. 1979. Priority pollutants. Environ. Sci. Technol. 13:416.

Kertesz-Saringer M, Morlin Z. 1975. On the occurrence of polycyclic aromatic hydrocarbons in the urban area of Budapest. Atmos. Environ. 9:331.

Ketseridis G, Hahn J, Jaenicke R, Junge C. 1976. Organic constituents of atmospheric particulate matter. Atmos. Environ. 10:603.

Kneip TJ, Eisenbud M, Kleinman MT, Bernstein DM, Lippman M, Riddick R. 1974. Trace Metals in Urban Aerosols. Second Annual Progress Report to the American Petroleum Institute and the Edison Electric Institute.

Lee RE, Goranson SS, Enrione RE, Morgan GB. 1972. National air surveillance cascade impactor network: II. Size distribution measurements of trace metal components. Environ. Sci. Technol. 6:1025.

Levin JO, Nilsson CA, Anderson K. 1977. Sampling of organic substances in workroom air with amberlite X+D-2 resin. Chemosphere 9:595.

Likens GE, Borman FH, Johnson NM, Pierce RS. 1967. The Ca, Mg, K and Na budgets for a small forest. Ecosystem Ecol. 5:772.

Louw CW, Richards JF, Faure PK. 1977. The determination of volatile organic compounds in city air by gas chromotography combined with standard addition, selective subtraction, IR and MS. Atmos. Environ. 11:703.

Lovelock JE, Maggs RJ, Wade RJ. 1973. Halogenated hydrocarbons in and over the Atlantic. Nature 241:194.

Lunde G, Bjorseth A. 1977. PAH in long-range transported aerosols. Nature 268:518.

Lunde G, Gether J, Gjos N, Lande M-BS. 1977. Organic micropollutants in precipitation in Norway. Atmos. Environ. 11:1007.

MacKay D. 1978. Volatilization of non-polar compounds from water surfaces, presented at US-EPA Workshop on Transport and Fate of PCBs in the Great Lakes, Grosse Ile, Michigan, April 3-4.

MacKay D, Leinonen PJ. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9:1178.

MacKay D, Yurn ATK. 1980. Transfer rates of gaseous pollutants between the atmosphere and natural waters. In: Atmospheric Input of Pollutants to Natural Waters, Eisenreich SJ, ed., Ann Arbor Science Pubs. (in press).

Mamuro T, Matsuda Y, Mizohata A, Matsunami T. 1971. Activation Analysis of Airborne Dust. Annual Rep. of the Radiation Center of Osaka Prefecture 12:1.

Mann JE, Enos HF, Gonzales J, Thompson JF. 1974. Development of sampling and analytical procedure for determining HCB, HCl, and 3-butadiene in air. Environ. Sci. Technol. 8:584.

Martin A, Barger FR. 1978. Some observations of acidity and sulphur in rainwater from rural sites in central England and Wales. Atmos. Environ. 12:1481.

McCall CS, Harriss RC. 1973. Precipitation and throughfall chemistry in the San Francisco Bay area. J. Environ. Qual. 7:352.

McClure VE, Lagrange J. 1977. Deposition of heavy chlorinated hydrocarbons from the atmosphere. Bull. Environ. Contam. Toxicol. 17:219.

Miguel AH, Friedlander SK. 1978. Distribution B(a)P and coronene with respect to particle size in Pasadena aerosols in the submicron-size range. Atmos. Environ. 12:2407.

Miles JW, Fetzer LE, Pearce GW. 1970. Collection and determination of trace quantities of pesticides in air. Environ. Sci. Technol. 4:420.

Moller J, Alfheim I. 1980. Mutagenicity and PAH analysis of airborne particulate matter. Atmos. Environ. 14:83.

Morrow NL, Brief RS. 1971. Elemental composition of suspended particulate matter in metropolitan New York. Environ. Sci. Technol. 5:786.

Moyers JL, Zoller WH, Duce RA, Hoffman GL. 1972. Gaseous bromine and particulate lead, vanadium, and bromine in polluted atmosphere. Environ. Sci. Technol. 6:68.

Moyers JL et al. 1973. Trace metal concentrations in the Tucson area atmosphere. Final Report to the Arizona Mining Association, Atmospheric Analysis Lab., Dept. of Chemistry, University of Arizona, Tucson.

Murphy TJ, Schinsky A, Paolucci G, Rzeszutko CP. 1980. Inputs of PCB from the atmosphere to Lakes Huron and Michigan. In: Atmospheric Input of Pollutants to Natural Waters, Eisenreich SJ, ed., Ann Arbor Science Pubs. (in press).

Murray KE. 1977. Concentration of volatiles on chromosorb 105. J. Chrom. Sci. 135:49.

National Research Council, 1979. Polychlorinated biphenyls. National Academy of Science, Washington, DC.

Nifong GD, Winchester JW. 1970. Particle size distributions of trace elements in pollution aerosols. Tech. Rep. ORA 08903-8-T, University of Michigan, Ann Arbor.

Nriagu JO, ed. 1979. Biogeochemistry of Mercury in the Environment. Elsevier-North Holland, New York.

O'Connors HB, Wurster CF, Powers CD, Biggs DC, Rowland RG. 1978. PCBs may alter marine trophic pathways by reducing phytoplankton size and production. Science 201:737.

Ohta T, Morita M, Mizoguchi I. 1976. Local distribution of chlorinated hydrocarbons in the ambient air in Tokyo. Atmos. Environ. 10:557.

Ohta T, Morita J, Mizoguchi I, Tada T. 1977. Washout effect and diurnal variation for chlorinated hydrocarbons in ambient air. Atmos. Environ. 11:985.

Olney EC, Bidleman TF. 1973. Atmospheric pollutant transport and deposition on the sea surface. Rep. to Department of Energy on Grant No. GX33777, University of Rhode Island, Kingston.

Orgill MM, Sehmel GA, and Peterson MR. 1976. Some initial measurements of airborne DDT over Pacific Northwest forests. Atmos. Environ. 10:827.

Peakall DB. 1976. DDT in rainwater in New York following application in the Pacific Northwest. Atmos. Environ. 10:899.

Pellizzari ED, Bunch JE, Berkley RE, MacRae J. 1976. Determination of trace hazardous organic vapor pollutants in ambient atmosphere by GC/MS. Anal. Chem. 48:803.

Penkett SA, Brice KA, Derwent RG, Eggleton AEJ. 1979. Measurement of CCl_3F and CCl_4 at Harwell over the period Jan. 1975-Nov. 1977. Atmos. Environ. 13:1011.

Persiani C. 1971. The detection of selected air pollutants using a laboratory neutron generator. Amer. Ind. Hyg. J. 32:573.

Petrenchuk OP, Selezneva ES. 1978. Chemical composition of precipitation in regions of the Soviet Union. J. Geophs. Res. 75:3629.

Pierce RC, Katz M. 1975. Dependency of PAH content on size distribution of atmospheric aerosols. Environ. Sci. Technol. 9:347.

Pilar S, Graydon WF. 1973. Benzene and toluene distribution in the Toronto atmosphere. Environ. Sci. Technol. 7:628.

Pillay KKS, Thomas CC. 1971. Determination of trace element levels in atmospheric pollutants by neutron activation analysis. J. Radioanal. Chem. 7:107.

Poltz K. 1970. Inorganic chemical analysis of non-polluted aerosols sampled at 1800 meters altitude. J. Geophys. Res. 75:2347.

Rahn KA. 1972a. Sources of trace elements in aerosols--an approach to clean air. Ph. D. Thesis, University of Michigan, Ann Arbor (University Microfilms 72-4956).

Rahn KA. 1972b. Study of the atmospheric aerosol on the Jungfraujoch. Progress Rep., Institut voor Nucleaire Wetenschappen, Rijksuniversiteit, Ghent, Belgium.

Rao AMM, Vohra KG. 1975. The concentrations of benzo(a)pyrene in Bombay. Atmos. Environ. 9:403.

Rappaport SM, Morales R. 1979. Air sampling and analytical method for 4,4' methylenebis (2-chloroaniline). Anal. Chem. 51:19.

Reiter R, Saldkovic R, and Potzl K. 1976. Chemical components of aerosol particles in the lower troposphere above central Europe measured under pure air conditions. Atmos. Environ. 10:841.

Robinson E, Rasmussen RA, Krasnec J, Pierotti D, Jakubovic M. 1977. Halocarbon measurements in the Alaskan troposphere and lower stratosphere. Atmos. Environ. 11:215.

Roberts RM. 1975. A review of some biological effects of lead emissions from primary and secondary smelters, presented to National Research Council of Canada, Ottawa, from Inst. for Environmental Studies, University of Toronto, Canada.

Sandalls FJ, Hatton DB. 1977. Measurements of atmospheric concentrations of trichlorofluoromethane, dichlorodifluoromethane and carbon tetrachloride by aircraft sampling over the British Isles. Atmos. Environ. 11:321.

Sanderson M, LaValle PD. 1979. Surface loading from pollutants in precipitation in southern Ontario: Some climatic and statistical aspects. J. Great Lakes Res. 5:52.

Schrimpff E, Thomas W, Hermann R. 1979. Regional patterns of contaminants in the snow of N. E. Bavaria. Water Air and Soil Poll. 11:481.

Seba DV, Prospero JM. 1971. Pesticides in the lower atmosphere of the northern equatorial Atlantic Ocean. Atmos. Environ. 5:1043.

Shriner DS. 1975. Effects of simulated rain acidified with sulfuric acid on host-parasite interactions. In: First International Symposium on Acid Precipitation and the Forest Ecosystem, Columbus, OH (NTIS PB-258695).

Simmonds PG, Kerrin SL, Lovelock JE, Shair FH. 1974. Distribution of atmospheric halocarbons in the air over the Los Angeles basin. Atmos. Environ. 8:209.

Sodergren A. 1972. Chlorinated hydrocarbon residues in airborne fallout. Nature 236:395.

Spencer WF, Cliath MM. 1975. Vaporization of chemicals, in Environmental Dynamics of Pesticides, Hague R, Freed VH, eds., Plenum, New York.

Stanley CW, Barney JE, Helton MR, Yobs AR. 1971. Measurement of atmospheric levels of pesticides. Environ. Sci. Technol. 5:430.

Stocks P, Commins BT, Aubrey KV. 1961. A study of polycyclic hydrocarbons and trace elements in smoke in Merseyside and other northern localities. Water Air Soil Poll. 4:141.

Strachan WMJ, Huneault H, Schertzer WM, Elder FC. 1980. Organochlorines in precipitation in the Great Lakes. In: Proceedings of International Symposium on Hydrocarbons in the Environment, Toronto, 1979.

Strand JW, Andren AW. 1978a. Organic carbon content of aerosols over Lake Michigan: Concentration, particle size distribution, and deposition. Rep. of the Water Chemistry Program, University of Wisconsin, Madison.

_________. 1978b. Polyaromatic hydrocarbons in aerosols over Lake Michigan: fluxes to the lake. Presented in the Environment Meeting, Battelle, Columbus, WA.

Sugimae A. 1975. Sensitive emission spectrometric method for the analysis of airborne particulate matter. Anal. Chem. 47:1840.

Sugimae A, Hasegawa T. 1973. Emission spectrographic determination of trace metals in airborne particulates collected on a membrane filter. Japan Analyst 22:3.

Suffet IH, ed. 1977. Fate of Pollutants in the Air and Water Environment. Wiley-Interscience, New York.

Swain WR. 1978. Chlorinated organic residues in fish, water and precipitation from the vicinity of Isle Royale, Lake Superior. J. Great Lakes Res. 4:398.

Swank WT, Henderson GS. 1976. Atmospheric input of some cations and anions: Forest ecosystems in North Carolina and Tennessee. Water Resources Res. 12:541.

Tarrant KR, Tatton JO'G. 1966. Organochlorine pesticides in rain water in the British Isles. Nature 219:725.

Tanner TM, Young JA, Cooper JA. 1974. Multi-element analysis of St. Louis aerosols by non-destructive techniques. Chemosphere 5:211.

Thomas JF, Mukar M, Tebbens BD. 1968. Fate of airborne benzo(a)-pyrene. Environ. Sci. Technol. 2:33.

Thrane KE. 1978. Background levels in air of lead, cadmium, mercury and some chlorinated hydrocarbons measured in south Norway. Atmos. Environ. 12:1155.

United Nations Scientific Committee on the Effects of Atomic Radiation. 1977. Sources and Effects of Ionizing Radiation. UNSCEAR Pub. 40, 32nd Session (A/32/40).

Versino B, deGroot M, Geiss F. 1964. Air pollution sampling by adsorption columns. Chromotographia 1:302.

Volchok HL. 1980. Atmospheric deposition of man-made radioactivity. In: Twelfth International Conference on Environmental Toxicity. Plenum, NY.

Warburton JA. 1973. The distribution of silver in precipitation from 2 seeded Alberta hailstorms. J. Appl. Meteorol. 12:677.

Weibel SR, Weidner RB, Cohen JM, Christianson AG. 1966. Pesticides and other contaminants in rainfall and runoff. J. Amer. Water Works Assoc. 58:1075.

Welles DE, Johnstone SJ. 1978. The occurrence of organochlorine residues in rain. Water Air Soil Poll. 9:271.

Wheatley GA, Hardman JA. 1965. Indications of the presence of organochlorine pesticides in rainwater in central England. Nature 207:486.

Wilkniss PE, Swinnerton JW, Lamontagne RA, Bressan DJ. 1975. Trichlorofluoromethane in the troposphere: Distribution and increase, 1971-1974. Science 187:832.

Williams FW, Umsted ME. 1968. Determination of trace contaminants in air by concentration on porous polymer beads. Anal. Chem. 40:2232.

Windom HL, Duce RA, eds. 1976. Marine Pollutant Transfer. Lexington Books, Lexington, MA.

Wright RF. 1976. The impact of forest fire on the nutrient influxes to small lakes in northeast Minnesota. Ecology 57:649.

Yasuda SK. 1975. Determination of MOCA in air. J. Chrom. 104: 283.

Young DR, McDermott DJ, Heesen TC. 1976. Aerial fallout of DDT in southern California. Bull. Environ Contam. Toxicol. 16:604.

Zafonte L, Hester NE, Stephens ER, Taylor OC. 1975. Background and vertical atmospheric measurements of fluorocarbon-11 and 12 over southern California. Atmos. Environ. 9:1007.

Zoller WH, Gordon GE. 1970. Instrumental neutron activation analysis of atmospheric pollutants utilizing GE(Li) ray detectors. Anal. Chem. 42:257.

Report of a Workshop on

SCREENING CHEMICALS FOR INADVERTENT MODIFICATION OF THE STRATOSPHERE

Boulder, Colorado
November 1979

Edited by
Daniel Albritton

PARTICIPANTS AND CONTRIBUTORS

Daniel L. Albritton
U.S. Dept. of Commerce
NOAA/ERL, R443
325 Broadway
Boulder, CO 80303
303-497-5785
FTS-320-5785

Julius Chang
Lawrence Livermore Lab.
P.O. Box 808
Livermore, CA 94550
415-422-4081
FTS-532-4081

Dieter Kley
U.S. Dept. of Commerce
NOAA/ERL, R448
325 Broadway
Boulder, CO 80303
303-497-3355
FTS-320-3355

Mack McFarland
U.S. Dept. of Commerce
NOAA/ERL, R448
325 Broadway
Boulder, CO 80303
303-497-3373
FTS-320-3373

Arthur L. Schmeltekopf
U.S. Dept. of Commerce
NOAA/ERL, R448
325 Broadway
Boulder, CO 80303
303-497-5340
FTS-320-5340

Jim Anderson
Harvard University
29 Oxford St.
Cambridge, MA 02138
617-495-5922

Carleton J. Howard
U.S. Dept. of Commerce
NOAA/ERL, R443
325 Broadway
Boulder, CO 80303
303-497-5820
FTS-320-5820

Shaw Liu
U.S. Dept. of Commerce
NOAA/ERL, R446
325 Broadway
Boulder, CO 80303
303-497-3356
FTS-320-3356

John M. Miller
NOAA/Air Resources Labs.
8060 13th Street
Silver Spring, MD 20910
301-427-7645
FTS-427-7645

William P. Wood
U.S. EPA
Office of Toxic Substances (TS-792)
Washington, DC
202-755-4860
FTS-426-0724

CONTENTS

Page

PARTICIPANTS AND CONTRIBUTORS 148

PREFACE 150

1. INTRODUCTION 151

2. METHODOLOGY 152

    2.1. Preliminary Analysis 152
    2.2. Tropospheric Removal Processes 152

        2.2.1. Photoabsorption 152
        2.2.2. Destruction by Reactive Tropospheric Species 154
        2.2.3. Scavenging by Atmospheric Aerosols 155
        2.2.4. Removal by Precipitation 155
        2.2.5. Dissolution Into the Oceans 155
        2.2.6. Surface Removal Processes 156

    2.3. Stratospheric Interaction 157

3. DATA REQUIREMENTS 158

    3.1. Gas Phase UV and Visible Absorption Spectra 158
    3.2. Destruction by Reactive Tropospheric Species 158
    3.3. Scavenging by Atmospheric Aerosols 159
    3.4. Removal by Precipitation 159
    3.5. Dissolution Into the Oceans 159
    3.6. Surface Removal Processes 160

4. DATA SOURCES 160

5. REFERENCES 160

APPENDIX: Sources of Physical and Chemical Data 163

PREFACE

In recent years an awareness has developed of the potential for human activities to affect the stratosphere. Activities over which concern has been raised because of their potential impacts on stratospheric ozone, one of the major constituents that absorb near-UV solar radiation, have included (a) the flights of high-altitude aircraft, such as the supersonic transport, which release nitrogen oxides into the stratosphere, (b) the operation of the Space Shuttle with attendant stratospheric emission of HCl gas, and (c) the use of chlorofluorocarbons (CFCs), which reach the stratosphere in significant quantities because of their stability at the earth's surface and in the troposphere. It has been postulated, on the basis of a great deal of laboratory and field data, that the stratospheric ozone layer may be modified by a variety of catalytic reaction cycles involving oxides of nitrogen, oxides of hydrogen, chlorine species, bromine species, and possibly other yet-unidentified reactants. The resulting modification of the stratospheric ozone layer by these catalytic cycles could have significant biological and agricultural impacts because of the extreme sensitivity of living organisms to the altered UV irradiation that would accompany a change in the stratospheric ozone shield.

Perception of the long-range consequences for humans and the biosphere has prompted a considerable expenditure of effort and resources by industry, academia, and several Federal agencies in quantifying the risks associated with activities of potential stratospheric significance.

The methodology described herein provides a means by which chemical substances may be evaluated to determine their potential to be transported into and affect the stratosphere (particularly the ozone in the stratosphere). The essence of the methodology is a step-by-step assessment of the capability of a number of processes to remove a substance from the atmosphere. The assessment begins with the tropospheric removal processes thought to be generally most significant, followed by those of somewhat lesser significance. In each case, any products formed in the troposphere are also assessed for their potential to reach the stratosphere.

SCREENING CHEMICALS FOR INADVERTENT MODIFICATION OF THE STRATOSPHERE

1. INTRODUCTION

The Environmental Protection Agency's initial involvement with potential ozone modification began in the fall of 1976 when the EPA announced the initiation of regulatory activities to control emissions of chlorofluorocarbons (CFCs). In March 1978 the EPA published regulations prohibiting the use of CFCs as propellants in aerosol products. The EPA derived its authority for such action from the Toxic Substances Control Act (TSCA), Public Law 94-469. As the Federal Agency charged with the administration of TSCA, the EPA is responsible for determining whether a new or existing substance presents or may present an unreasonable risk of injury to health or to the environment.

In addition, passage of the Clean Air Act Amendments of 1977, Public Law 95-95, assigned EPA specific aspects of the responsibility for protecting the stratosphere, especially the ozone in the stratosphere. Part B of the amended Clean Air Act provides that substances, practices, processes, and activities that may affect the stratosphere, especially ozone in the stratophere, should be investigated by the Administrator of the EPA to give early warning of any potential problem and to develop the basis for possible future regulatory action. The Administrator is required to conduct studies and research concerning the effects of such substances and activities, to report biennially to Congress the results of these studies and research, to report annually to Congress recommendation for control, and to propose regulations for the control of any substance or activity that may reasonably be anticipated to affect the stratosphere.

Because of the EPA's need to determine, often within a relatively short time and with limited data, the potential stratospheric importance of both new and existing chemicals, a methodology for the systematic examination of chemical substances is required. The methodology (1) must evaluate the potential of a substance to enter the atmosphere; (2) must account systematically for each of the potential physical and chemical mechanisms by which a substance may be removed from the atmosphere at the earth's surface and in the troposphere, and must account for any reaction products formed by these physical and chemical removal processes; and, finally (3) must assess the potential for stratospheric modification.

2. METHODOLOGY

The methodology described herein provides a means by which chemical substances may be evaluated to determine their potential to be transported into and affect the stratosphere (particularly the ozone in the stratosphere). The essence of the methodology is a step-by-step assessment of the capability of a number of processes to remove a substance from the atmosphere (Figure 1). The assessment begins with the tropospheric removal processes thought to be generally most significant, followed by those of somewhat lesser significance. In each case, any products formed in the troposphere are also assessed for their potential to reach the stratosphere.

2.1. Preliminary Analysis

A prelude to the application of this methodology is the determination that an expected significant transport of a substance into the atmosphere is based upon a consideration of (1) materials balance data (i.e., production, use, and disposal information), (2) environmental characterization data (i.e., meteorological, hydrological, and topographical information), and (3) materials data (i.e., physical state and chemical properties).

2.2. Tropospheric Removal Processes

The following tropospheric removal processes should then be considered:

2.2.1. Photoabsorption

It is first necessary to establish whether a substance absorbs radiation in the spectral range between 2950 and 7000 Å. This constitutes the spectral region of concern because light at shorter wavelengths is absorbed above the tropopause, and radiation of longer wavelengths is not of sufficient energy to dissociate chemical bonds of interest here. If photodissociation is predicted, that molecule may be eliminated from consideration, provided that the quantitative criteria discussed below are met. However, identical criteria must be applied to the potential products of that dissociation. Furthermore, if photodissociation is predicted to lead to enhanced chemical reactivity of the dissociation products, then further reactive cycles must be considered as possible loss processes.

The primary quantity of concern for a quantitative assessment of photoabsorption is the product of the solar flux and the absorption cross section at each wavelength and at each altitude such that the photodissociation rate can be determined:

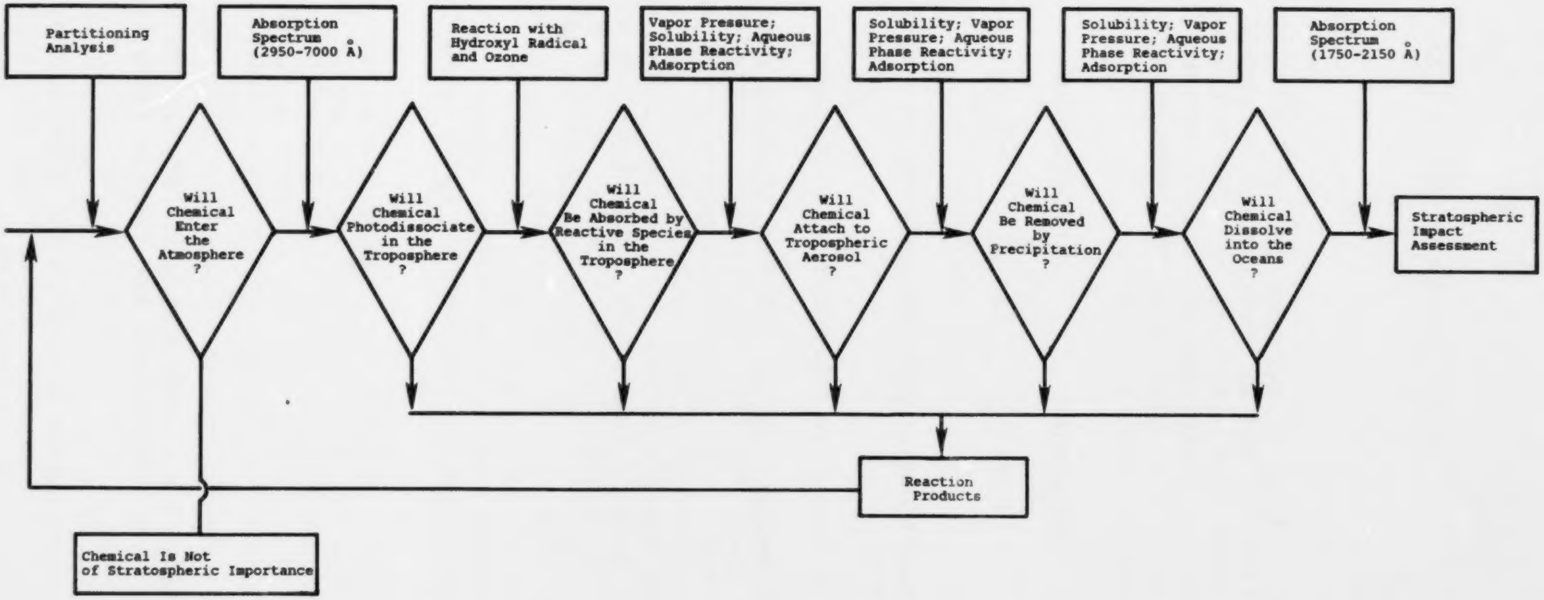

Partitioning Analysis
Absorption Spectrum (2950-7000 Å)
Reaction with Hydroxyl Radical and Ozone
Vapor Pressure; Solubility; Aqueous Phase Reactivity; Adsorption
Solubility; Vapor Pressure; Aqueous Phase Reactivity; Adsorption
Solubility; Vapor Pressure; Aqueous Phase Reactivity; Adsorption
Absorption Spectrum (1750-2150 Å)
Will Chemical Enter the Atmosphere ?
Will Chemical Photodissociate in the Troposphere ?
Will Chemical Be Absorbed by Reactive Species in the Troposphere ?
Will Chemical Attach to Tropospheric Aerosol ?
Will Chemical Be Removed by Precipitation ?
Will Chemical Dissolve into the Oceans ?
Stratospheric Impact Assessment
Reaction Products
Chemical Is Not of Stratospheric Importance

Figure 1. Schematic of methodology for identifying chemicals of stratospheric importance.

$$J(z) = \int_{2950\mathring{A}}^{7000\mathring{A}} F(\lambda)\sigma(\lambda)\ \exp\ (-T(\lambda,z))d\lambda,$$

where $F(\lambda)$ is the solar flux in photons $cm^{-2}s^{-1}\ \mathring{A}^{-1}$, $\sigma(\lambda)$ is the absorption cross section in cm^2 at wavelength λ, and $T(\lambda,z)$ is the atmospheric opacity above the altitude z. The critical quantity is the constituent mixing ratio, which, when combined with the relevant production term P(z) provides the information needed to calculate the tropospheric mixing ratio:

$$[X]/[M] = \int_{0}^{tropopause} P(z)dz \Bigg/ [M] \int_{0}^{tropopause} J(z)dz,$$

where [X] is the released substance concentration and [M] is the total concentration.

2.2.2. Destruction by Reactive Tropospheric Species

This destruction mechanism is limited to homogeneous gas phase reactions that occur in the tropopause. Although tropospheric chemistry is not well understood, many reactions of several important reactive species, such as $O(^3P)$, $O(^1D)$, O_3, NO, NO_2, OH, and HO_2, have been studied. There are other species that undoubtedly play a very important role, but few of their reaction rate constants are measured. These include NO_3, alkoxy, and alkylperoxy radicals. At the present time only two of these species, the hydroxyl radical OH and ozone O_3 are known to be significant scavengers of chemical substances in the atmosphere. Chemical substances containing hydrogen are generally reactive toward OH; others containing double bonds, specifically olefins, are reactive toward both OH and O_3.

The atmospheric lifetime t of a chemical substance S toward destruction by some species A is defined as the reciprocal of the first-order rate constant for the reaction of S with A. If that reaction is bimolecular, then $t = 1/k[A]$, where k is the bimolecular rate constant and [A] is the atmospheric concentration of A. If the reaction is termolecular, then $k = k^{III}\ [M]$, where k^{III} is the termolecular rate constant and [M] is the effective concentration of air. Few reactions are purely termolecular in the troposphere.

If a chemical substance is found to be degraded by reaction with some species, then the possibility of the formation of persistent products must also be evaluated.

2.2.3. Scavenging by Atmospheric Aerosols

Another possible tropospheric removal process is scavenging by aerosols, which are subsequently removed from the atmosphere by dry deposition or wet removal.

The aerosol residence times in the troposphere are estimated to be from 5 to 15 days (Junge 1977, Moore et al. 1973, Slinn et al. 1978). The gas kinetic collision frequency of molecules with aerosols is in the range of 10^{-2} to 1 per second. If the sticking coefficient (the fraction of the molecules that stays on the aerosol following each collision) of a substance is, for example, 10^{-5}, then its tropospheric lifetime is 10^{5} to 10^{7} s.

The physical property of a substance that is of primary significance in determining its sticking coefficient with aerosols is its vapor pressure. Junge (1977) has developed a model to estimate the partial atmospheric removal rate of substances by this process as a function of vapor pressure. According to Junge's model, substances with vapor pressures greater than approximately 10^{-6} torr would have partial residence times of the order of days and would be removed effectively by this process. In addition, substances with a high solubility, or a high reactivity in the dissolved phase, may also be scavenged effectively by aerosols.

2.2.4. Removal by Precipitation

Three properties of a substance are important in evaluating its removal by precipitation--solubility, dissociation in water, and oxidation in water. In mass transfer of a substance, a gas to a cloud or rain droplet, the highly soluble gas is quickly absorbed. If further dissociation takes place in removal of a substance, it reduces the chances of release back into the atmosphere. Aerosol removal also depends on the solubility of a given aerosol and its ability to act as a condensation nucleus or dissolve into a cloud or rain droplet. A detailed description of these processes is given in the workshop report on Toxic Substances in Atmospheric Deposition.

2.2.5. Dissolution Into the Oceans

Another heterogeneous removal process is the dissolution of substances into the oceans. The solubility of a substance is of primary concern regarding this removal mechanism. However, because of the relatively slow mixing of the surface water above the thermocline with the deep ocean (exchange time is approximately 15 years; Panel on Atmospheric Chemistry 1976), for dissolution into the oceans to be significant it must be followed by the removal of the substance by reaction in the liquid phase (e.g., oxidation, hydrolysis, dissociation, biological action, etc.).

In an analysis of atmospheric removal processes, Slinn et al. (1978) showed that the transfer rate of highly soluble (solubility, $\alpha > 10^2$) or reactive substances from the atmosphere into the oceans is controlled by the rate at which the substance is transferred through the atmosphere to the ocean surface (gas transfer rate). The vertical gas transfer rate is approximately 1 $cm\,s^{-1}$ for low molecular weight gases and is slightly slower for high molecular weight gases. If the height over which the substance is distributed is 10 km, the corresponding tropospheric lifetime of the substance is approximately 10 days.

For substances of lower solubility ($\alpha < 10^2$), transfer of the substance from the atmosphere to the ocean is controlled primarily by the liquid phase transfer rate. A lower limit to the lifetime of these substances ($\alpha < 10^2$) can be estimated using a relationship developed by Broecker and Peng (1974). This estimated lifetime is a lower limit because it is assumed in the derivation of the relationship that the flux of the substance from the ocean to atmosphere is zero; i.e., the effective concentration of the substance in the ocean is zero. The relationship is

$$\text{Lifetime} = \frac{2.3 \times 10^8}{\alpha} \text{ seconds,}$$

where α is the solubility (volume of gas at STP absorbed by one volume of water when the pressure of the gas above the water is 1 atm) of the substance. Therefore, for the tropospheric lifetime to be less than a year, α must be greater than 7. For gases like O_2, N_2, CH_4 CO and Ar; $\alpha \simeq 0.02$.

Factors such as chemical reaction of the dissolved substance and solution pH can lead to an enhanced solubility coefficient (Junge 1963) for the substance. For example, Hales and Sutter (1973) have shown the effect that solution pH has on the dissolution of SO_2.

The substance can be removed from the dissolved phase by dissociation, hydrolysis, or oxidation. If any of these potential reaction pathways for a substance is identified as being feasible, the reaction rates should be quantified so that the significance of that pathway for the removal of that substance from the dissolved phase (and hence, the atmosphere) can be assessed.

2.2.6. Surface Removal Processes

There is very little information on surface removal processes. Only one has had much attention. The possibility that the photoabsorption cross section of a substance will be modified when it is physically adsorbed on a surface has been studied for some of the chlorofluorocarbons adsorbed on sand (Ausloos et al. 1977). If this enhanced photoabsorption leads to excitation of dissociation, the possibility exists for tropospheric removal by this process.

2.3. Stratospheric Interaction

If no significant tropospheric removal mechanism can be identified for the substance of interest, then continued accumulation of the substance in the troposphere will definitely lead to significant transport into the stratosphere and beyond. It is reasonable to expect that the substance will begin to photodissociate above some altitude. Furthermore, this substance and its derivatives most likely will react with some radicals in the stratosphere. Consequently any impact analysis must be extensive and draws upon all the available information on stratospheric chemistry.

If the tropospheric removal for the substance gives lifetime of τ, then the maximum fraction of the substance dissociated in the stratosphere can be determined by assuming that all of the substance that is transported to the stratosphere gets dissociated there. Thus, the exchange process between the troposphere and the stratosphere will determine the maximum fraction.

The average exchange time for stratospheric air with the troposphere is about 15 years. Since the troposphere contains about four times as much air as the stratosphere, the lifetime of the substance against the stratospheric sink is 6 years. Consequently, the lifetime of the substance against the tropospheric and stratospheric removal is

$$\frac{1}{\frac{1}{\tau} + \frac{1}{6}} = \frac{6\tau}{\tau+6} \text{ years.}$$

Therefore, the maximum fraction of the substance dissociated in the stratosphere is

$$\frac{6\tau}{\tau+6} / 6 = \frac{\tau}{\tau+6} .$$

Since the amount of stratospheric ozone is maintained primarily through the interaction of several photochemical catalytic cycles the introduction of any substance that either directly or indirectly interacts with chemical species involved in these cycles will certainly affect the ozone layer. Several well-known families of hydrogen-, nitrogen-, and chlorine-containing molecules are (H, HO, HO_2, H_2O_2), (N, NO, NO_2, NO_3, N_2O_5, HNO_3, HNO_4) and ($C\ell$, $C\ell O$, $HC\ell$, $HOC\ell$, $C\ell ONO_2$). Therefore, a simple guideline for assessing potential impact on stratospheric ozone of any substance would be to study the reactivity of it or its derivative substance with these molecules. Any significant reaction that may affect the balance of any family will lead to significant impact on the ozone layer. Furthermore, reactions with the so-called source molecules such as CH_4, N_2O, H_2O, $CH_3C\ell$, $CC\ell_4$, $CH_3CC\ell_3$, etc., will also be of importance. In addition to the chemical interaction, one must also consider the potential impact on the radiative and dynamic aspect of stratospheric climatology, which further complicates the impact analysis.

3. DATA REQUIREMENTS

The proposed stratospheric impact assessment methodology consists of a sequence of steps in which certain properties of a substance are compared with evaluation criteria to determine the significance of each of a series of potential removal mechanisms or sinks. A number of sources may be utilized in obtaining the data and information required to assess the tropospheric removal of chemical substances. Data for existing substances may be available from data banks of chemical properties, which are accessible in the literature; data for new and existing substances may be obtained from industry through testing required under TSCA; and physical or chemical properties of both new and existing of both new and existing substances may be estimated from data that are available for structurally similar chemicals. Test methodologies and/or data sources are discussed here in terms of the removal processes.

3.1 Gas Phase UV and Visible Absorption Spectra

It is recommended to EPA that the gas phase ultraviolet and visible absorption cross sections be measured for each constituent throughout the 2950 to 7000 Å wavelength interval. A continuous scan survey of 15 Å resolution is adequate for initial appraisal. Sample pressure, temperature, and relative humidity should be varied over the range of conditions found in the troposphere. It must be recognized that in many cases such measurements require an advanced level of experimental capability and that generalized procedures may be misleading. References cited for consultation regarding the measurement techniques are Chou et al. (1978), Tsubomura et al. (1964), Gordus and Bernstein (1954), Lacher et al. (1950), and Calvert and Pitts (1977). Extensive appraised cross sections appear in two recent NASA publications edited by DeMore et al. (1979) and Hudson and Reed (1980).

3.2 Destruction by Reactive Tropospheric Species

There are, at present, no simple procedures for experimental evaluation of the atmospheric reactivity of gaseous chemicals. The information that is needed to evaluate the importance of destruction of a substance by a particular tropospheric species includes (1) knowledge of the atmospheric concentration of the species [A], and (2) knowledge of the rate constants k for the reaction of the atmospheric species with the chemical substance under conditions of temperature, pressure, relative humidity, etc., relevant to the troposphere.

Accurate calculation of the tropospheric lifetime requires knowledge of [A] and k throughout the troposphere for all seasons; however, for the present purpose, it is adequate to use globally averaged quantities. The tropospheric concentration profiles of most reactive species are sufficiently uncertain to allow a global average to be used. Further, the only significant tropospheric variable associated with nearly all rate constants is temperature. It is recommended that for estimating the lifetimes of chemical substances in the troposphere, $t = 1/k[A]$, the following quantities be used: $k = \underline{k}(265K)$, $[OH] = 5 \times 10^{5}$ molecule cm^{-3}, and $[O_3] = 7 \times 10^{11}$ molecule cm^{-3}. Rate constant data should be taken from standard references such as Atkinson et al. (1979), Hudson and Reed (1979), and Baulch et al. (1980). When rate constant data are not available, estimation methods such as those given by Hendry and Kenley (1979) may be used. These estimates consider the principal mechanisms by which hydroxyl radicals and ozone attach chemical substances and assume that similar structural characteristics in different molecules will have the same reactivity toward such attack. On the basis of known rates of reaction for processes such as hydrogen atom abstraction, addition to olefinic bonds and addition to aromatic rings, reasonable estimates of reaction rate constants for substances with similar structural features can be made.

3.3 Scavenging by Atmospheric Aerosols

Vapor-aerosol partitioning in the atmosphere depends on the vapor pressure of the organic compound, the size and surface area of the suspended particulates, and the organic content of the aerosol. For vapor-aerosol distributions calculated from vapor pressure and the quantity of atmospheric particulates see the workshop report on Toxic Substances in Atmospheric Deposition.

3.4 Removal by Precipitation

Wet removal of vapors is governed by the Henry's law constant H, which can be calculated as the ratio of the substance's vapor pressure to solubility. Washout ratios calculated as the reciprocal of H are given for a number of substances in the workshop report on Toxic Substances in Atmospheric Deposition.

3.5. Dissolution Into the Oceans

Methods for calculating the flux of a chemical to a water body have been described in the workshop report on Toxic Substances in Atmospheric Deposition.

3.6. Surface Removal Processes

The vapor pressure of a substance bears upon this poorly characterized removal process, but it is difficult to express a quantitative relationship.

4. DATA SOURCES

Numerous sources of required data are available in the published literature, and privately maintained data bases may be purchased. A partial summary of sources of visible and ultraviolet absorption spectra, vapor pressure, and solubility data is presented in the Appendix. For those substances for which data are not available, the required information often can be estimated on the basis of structure-correlation relationships and similarities to substances for which data are available. Provided that the specific chemical identity (molecular composition and structure) is known, the photochemical and chemical reactivity of some substances can be estimated according to methods developed by Hendry and Kenley (1979). Other physical and chemical properties of primary importance to determining stratospheric significance by the proposed methodology can also be estimated.

Numerous methods for estimating environmentally important physical and chemical properties of chemicals are available in the published literature (Reid et al. 1977; Arthur D. Little, Inc. 1978; Lyman 1978).

5. REFERENCES

Arthur D Little, Inc. 1978. Study performed for the US Army Medical Bioengineering Research and Development Laboratory.

Atkinson R, Darnall KR, Lloyd AC, Winer AM, Pitts JN, Jr. 1979. Kinetics and mechanisms of the reaction of the hydroxyl radical with organic compounds in the gas phase. In: Advances in Photochemistry, Vol. 11, pp. 375-488, John Wiley and Sons, New York, NY.

Ausloos P, Tebbert RE, Glasgow L. 1977. Photodecomposition of chloromethanes adsorbed on silica surfaces. J. Res. Natl. Bur. Stds. 82:1.

Baulch DL, Cox RA, Hampson RF, Jr., Kerr JA, Troe J, Watson RT. 1980. Evaluated kinetic and photochemical data for atmospheric chemistry. J. Phys. Chem. Ref. Data 9:295-471.

Broecker WS, Peng TH. 1974. Gas exchange rates between air and sea. Tellus 26:21-35.

Calvert JG, Pitts JN. 1966. Photochemistry. John Wiley and Sons, New York, NY.

Chou CC, et al. 1978. Stratospheric photodissociation of several saturated perhalochlorofluorocarbon compounds in current technological use. J. Physical Chem., 82:1.

DeMore WB, ed. 1979. Chemical, kinetic and photochemical data for use in stratospheric modeling. Jet Propulsion Laboratory Pub. 79-29, Pasadena CA.

Gordus AA, Berstein RB. 1954. Isotope effect in continuous ultraviolet absorption spectra. J. Chemical Phys. 22(5):290-295.

Hales JM, Sutter SL. 1973. Solubility of sulfur dioxide in water at low concentrations. Atmospheric Environment 7:997-1001.

Hendry DG, Kenley RA. 1979. Atmospheric reaction products of organic compounds. EPA-560/12-79-001 report, U.S. Environmental Protection Agency, Washington DC.

Hudson RD, Reed EI, eds. 1979. The stratosphere: present and future. NASA Ref. Pub. 1049, Washington, DC.

Junge CE. 1963. Air chemistry and radioactivity. Academic, New York, NY.

Junge CE. 1977. Fate of global pollutants. In: Fate of Pollutants in the Air and Water Environments, Part 1, Suffet IH, ed., John Wiley and Sons, New York, NY.

Lacher JR, et al. 1950. The near ultraviolet absorption spectra of some fluorinated derivatives of methane and ethylene. J. American Chemical Soc. 72:5486-5489.

Lyman WJ. 1978. Paper presented at the 1978 Spring Meeting of the American Chemical Society, Anaheim, CA.

Moore HE, Poet SE, Martell EA. 1973. 222Rn, 210Pb, 210 Bi, and 210P profiles and aerosol residence times versus altitude. J. Geophys. Res. 78:7065-7075.

Panel on Atmospheric Chemistry of the National Research Council. 1976. Halocarbons: Effects on stratospheric ozone. National Academy of Sciences, Washington, DC.

Reid RC, Prausnitz JM, Sherwood TS. 1977. The properties of gases and liquids, their estimation and correlation. Third Edition, McGraw-Hill, New York, NY.

Slinn WGN, et al. 1978. Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. Atmospheric Environment 12:2055-2087.

Tsubomura H, et al. 1964. Vacuum ultraviolet absorption spectra of saturated organic compounds with non-bonding electrons. Bull. Chem. Soc. Japan 37:417-423.

APPENDIX:

Sources of Physical and Chemical Data

Ultraviolet Absorption Spectra

(1) Sadtler Research Laboratories, Inc.
3316 Spring Garden Street
Philadelphia, PA 19104
215/382-7800
Contact -- Alen Bloom

Sadtler publishes data bases of chemical UV spectra. The following data bases are available:

(a) Standard UV spectra;
(b) Pharmaceutical UV spectra;
(c) Biochemical UV spectra;
(d) Commonly abused drugs UV spectra; and
(e) Prepared and prescription drugs UV spectra.

Each data base provides UV absorption spectra of the chemicals included and indices for accessing the spectral information. Data are indexed alphabetically for chemical name, chemical class, molecular formula, and UV absorption locator.

(a) Standard UV spectra. Now comprises 102 volumes, each containing approximately 500 spectra of pure chemical compounds. Current price: $135 per volume plus $500 for the complete index (Total = $14,300). Four additional volumes of new spectra are added each April.

(b) Pharmaceutical. Now comprises 4 volumes with a total of 2,000 spectra. The materials included are pharmaceuticals, and therefore, may be composed of one or several pure chemicals. Total price is $964, including index.

(c) Biochemical. Now comprises 2 volumes with a total of 650 spectra. Total cost is $324, including index.

(d) Abused drugs. Now comprises 1 volume with 300 spectra. Total cost is $318, including index.

(e) Prepared and prescription drugs. Now comprises 2 volumes with a total of 600 spectra. Total cost is $293, including index.

Unlike data base 1, data bases 2 through 5 are not updated annually. Rather, they may be updated by occasional issuing of a new volume.

All prices are subject to a price increase of approximately 10% in September 1979.

(2) The Thermodynamics Research Center
Data Distribution Office
Texas A & M Research Foundation
F.E. Box 130
College Station, Texas 77843
713/846-8765
Contact -- Dr. Wilhoit

Publishes tables of thermodynamic and physical property data (including vapor pressure) and spectral data (including UV) in the form of loose-leaf data sheets.

Approximate costs of data files are:

Thermodynamic and physical property data -- $1,200.
Spectral data -- $400.

Supplements are issued twice each year for the thermodynamic and physical property tables and at irregular intervals for the spectral data.

TRC is building a computer data file that can be accessed by remote terminal. The only costs for these data would be the nominal computer charges by the University Data Processing Center.

(3) Phillips JP, Feuer H, Thyagarajan BS (Eds.). 1945-1970. Organic Electromagnetic Spectral Data. Volumes 1-12, John Wiley and Sons, New York, NY.

Gives ultraviolet-visible spectra of over 250,000 organic compounds.

(4) DMV. UV Atlas of Organic Compounds. (Butterworths), 1966-1971, Volumes 1-5, Plenum Press, New York, NY.

Gives spectra of approximately 1,500 compounds.
Cost: $65 per volume.

(5) Hirayama K. 1967. Handbook of Ultraviolet and Visible Absorption Spectra of Organic Compounds. Plenum Press, New York, NY.

(6) Friedel RA, Orchin M. 1951. Ultraviolet Spectra of Aromatic Compounds. John Wiley & Sons, New York, NY.

Gives spectra of 579 compounds.

(7) All-Union Synthetic Rubber Research Institute. 1966. Ultraviolet Spectra of Elastomers and Rubber Chemicals, Plenum Press, New York, NY.

Gives spectra of 141 compounds.

(8) Calvert JC, Pitts JN. 1967. Photochemistry. Second Edition, Wiley and Sons, New York, NY.

Photochemical and Reaction Rate Data

Baulch DL, Cox RA, Hampson RF Jr., Kerr JA, Troe J, Watson RT. 1980. Evaluated kinetic and photo chemical data for atmospheric chemistry. J. Phys. Chem. Ref. Data, 9:295-471.

Solubility

(1) Linke WF. 1965. Solubility of Inorganic and Metal-Organic Compounds, Volumes I and II, Fourth Edition, 1965, American Chemical Society, Washington, D.C.

Gives solubilities, in g/100 g solution, of approximately 5,000 compounds.
Index in Volume II.
Cost: Approximately $80.

(2) Stephen H, Stephen T. 1963. Solubilities of Inorganic and Organic Compounds, Volume I, Parts 1 and 2. Pergamon Press, New York, NY.

Gives solubilities, in wt. % or g/liter, of over 2,000 compounds. Index in Part 2.

(3) National Academy of Engineers. 1972. CAChe Physical Properties Book. Washington, D.C.

(4) JANAF Thermochemical Tables. Published in looseleaf form, updated yearly.

Vapor Pressure

(1) Thermodynamics Research Center

See entry under Ultraviolet Spectra.

(2) Thermodynamics Research Center. 1978. Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds.

Gives vapor pressure of over 700 compounds. Doubly indexed -- alphabetically according to subject index of Chemical Abstracts and by boiling point.

(3) Weast RC (Ed.). 1979. Handbook of Chemistry and Physics. Chemical Rubber Co., Cleveland, OH.

Gives vapor pressure of inorganic (≈350) and organic (≈1,000) compounds.

(4) Dreisbach RR. 1952. Pressure - Volume - Temperature Relationships of Organic Compounds. Handbook Publishers, Inc., Sandusky, OH.

Gives vapor pressure data on compounds in 23 families of organic chemicals.

(5) Jordan TE. 1954. Vapor Pressure of Organic Compounds. Interscience Publishers, New York, NY.

Gives vapor pressure of 1,492 chemicals. Indexed alphabetically and by family.

(6) JANAF Thermochemical Tables.

See Solubility References.

Report of a Workshop on

THE IMPACT OF CHEMICALS ON THE RADIATIVE TRANSFER IMBALANCE

Boulder, Colorado
September 1979

Edited by
John J. DeLuisi

PARTICIPANTS AND CONTRIBUTORS

Thomas Ackerman
Space Science Division
NASA - Ames Research Center
Moffett Field, CA 94035

Marshall Atwater
Center for the Environment & Man
275 Windsor Street
Hartford, CT 06120

Robert Charlson
Dept. of Civil Engineering
Water and Air Resources
University of Washington
Seattle, WA 98195

John J. DeLuisi - Convener
U.S. Dept. of Commerce
NOAA/ERL/ARL/GMCC, RF3292
325 Broadway
Boulder, CO 80303

James Friend
Drexel University
32nd and Chestnut
Philadelphia, PA 19104

James Hansen
Institute for Space Studies
GSFC-NASA
New York, NY 10025

Kirby Hanson
U.S. Dept. of Commerce
NOAA/ERL/ARL/GMCC, RF3292
325 Broadway
Boulder, CO 80303

John Miller
NOAA/ERL/ARL, R32
Silver Spring, MD 10910

Rudolph Pueschel
U.S. Dept of Commerce
NOAA/ERL, R31
325 Broadway
Boulder, CO 80303

Hal Rosen
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

William P. Wood
Office of Toxic Substances
U.S. EPA   (TS-792)
401 M Street, S.W.
Washington, D.C. 20460

CONTENTS

Page

PARTICIPANTS AND CONTRIBUTORS 168

PREFACE 170

1. INTRODUCTION 171

2. CRITERIA FOR DETERMINING SIGNIFICANT RADIATIVE EFFECTS 172

3. GASES AND SECONDARY PRODUCTS 173

    3.1. Reaction With Atmospheric Constituents 175
    3.2. Gas-Particle Transformations 176

4. PARTICLES 176

    4.1. Direct Effects 176
    4.2. Indirect Effects 179

5. THE EFFECT OF CHEMICALS ON THE OPTICAL PROPERTIES OF CLOUDS 179

    5.1. The CCN Problem 180
    5.2. The Absorption Problem 182

6. REFERENCES 184

APPENDIX: Atmospheric Chemical Processes 187

PREFACE

This workshop was given the task of delineating the significant factors, possessed by any chemical, that may directly or indirectly affect the radiation balance of the atmosphere. Atmospheric physics research has already given information on direct and indirect effects. An example of direct effect is the cumulative infrared greenhouse effect of several trace gases, some of which are anthropogenic (Wang et al. 1978), and the short wave radiative effects of unactivated aerosol particles in clouds (Ackerman and Baker 1977). Examples of indirect effects are those of aerosols as they change cloud droplet size distributions and hence albedo and radiative properties (Twomey 1976), and as found in observations of albedo and absorption anomalies in clouds (Robinson 1958), and cloud modification by urban pollution (Barrett et al. 1979).

THE IMPACT OF CHEMICALS ON THE RADIATIVE TRANSFER IMBALANCE

1. INTRODUCTION

There are several general factors that have a bearing on whether a chemical will have a significant effect on the radiation balance. These factors may be posed as questions:

(1) Does the chemical strongly absorb infrared or visible radiation?
(2) Will great quantities of the chemical be released to the atmosphere?
(3) Does the chemical possess efficient water/ice particle nucleation properties, and
(4) Does the chemical possess catalytic properties that will influence/alter gas-to-particle conversion processes which ultimately affect the radiation balance?
(5) Is the expected lifetime of the chemical long (years) or short (days)?

It is obvious that these factors are not independent of each other. For example, a very minute amount of a trace gas having powerful infrared radiative properties (1) may influence the radiation balance; on the other hand, large quantities of gas (2) with extended lifetime (5) and with small infrared radiative properties might produce a similar effect. It is conceivable that (1) may be influenced by (4) which results in efficient ice nucleating material (3). In this report we do not consider photochemical influence on natural gases (primarily ozone) since it has been the subject of another workshop.

The Appendix describes a comprehensive organized scheme of atmospheric chemical processes which covers all aspects of the source-sink fate of any chemical introduced into the atmosphere. There is a need to consider the short lifetimes of chemicals in certain intermediate states which may also play an important role in determining the ultimate effect on the radiation balance.

An absolute reference does not exist from which to define significant radiative effects. Any concentration of any substance will have an effect on the radiation field, although it may be physically imperceptible and climatologically insignificant as well. Consequently, the need for a reference scale stimulated workshop participants to adopt a set of criteria based upon a prespecified perturbation to atmospheric temperature including its dependence on a spatial scale. The current set of criteria is subject to change with new results from modeling and experimental efforts since the state of the art in our understanding of radiation and climate is not well advanced.

With regard to the potential effect of industrial chemicals, it is important to maintain a perspective of what is possible and what is probable. It is highly possible that a chemical may possess some adverse radiative property, but the question that must follow is whether a sufficient amount will be released to produce a significant effect. The probability of this happening is undoubtedly low. There is a greater, but still low, probability that the radiative effects of several or more substances may combine in a cumulative way to produce a non-negligible temperature perturbation. Cumulative effects can be estimated to a first approximation by simple addition of the individual temperature perturbation of each substance released. No specific recommendation was given by the panel for action to be taken if in a particular circumstance the potential exists for a significant cumulative effect. However, it would seem reasonable to maintain an inventory on those released substances having potentially significant radiative effects in order to reduce the chance of being caught unaware of the situation.

The sections that follow represent a consensus of experts in the fields of aerosol chemistry and physics, atmospheric gas chemistry, atmospheric radiative transfer and thermodynamical processes, and aerosol optical properties.

2. CRITERIA FOR DETERMINING SIGNIFICANT RADIATIVE EFFECTS

Anthropogenic chemical products released in the atmosphere, both gases and aerosols, are potentially capable of absorbing solar and/or terrestrial thermal radiation and thereby affecting the atmospheric temperature and climate. Furthermore, it is necessary to consider not only primary pollutants (chemicals released into the atmosphere), but also secondary products which may be formed by transformation of the primary pollutant. Estimates of effects of secondary products must be based on our current knowledge of atmospheric chemistry. Since there is still much to be desired in our understanding of gas-to-particle-formation chemistry, we can expect changes in such estimates as our knowledge grows.

The magnitude of radiative impact that constitutes a significant threat depends upon the horizontal scale over which the change in atmospheric composition is effective. Changes that are global in scale, as in the case of chemicals with a tropospheric lifetime of years or longer, require a relatively smaller radiative impact to yield a significant climate change. On the other hand, regional and local changes must be relatively large in order to be significant compared with natural variability and with other known or anticipated effects of human activity.[1]

---

[1] The panel acknowledges the fact that the global climatic effects of anthropogenic pollutants (despite the tremendous amounts released to the atmosphere) are still under debate.

For those released constituents or atmospheric modifications that will be global in extent, the threshold level for a significant temperature effect is ~0.1-0.5 K. This is based primarily on the fact that the variation of global temperature over the last century, which has witnessed significant climate variation, is ~0.5 K (cf. Figure 1). In addition, climate models suggest that the largest human-induced climate impact during the next few decades will be due to increasing atmospheric CO_2, and will be of this order of magnitude. For dispersals on a synoptic scale the magnitude for a significant temperature impact is ~0.5-2 K (Ball and Robinson 1979), as a result of the larger natural variability on such a scale. For a local dispersal, e.g., over a given city, the change required for a substantial impact is ~1-5 K (Clarke 1969; Atwater 1975, 1977).

These temperature criteria can be converted to specifications on gaseous, aerosol, or cloud properties by employing simple radiative models that give order-of-magnitude estimates of the temperature change accompanying a given change in atmospheric composition. As a uniform basis of comparison the radiative/convective temperature profile models, as described by Manabe and Wetherald (1967), Wang et al. (1978) and Ramanathan and Coakley (1978), can be used. These models are reasonably consistent; for example, they yield a warming of ~2 K for a doubling of atmospheric CO_2. In fact, more complex models of the climate system generally agree with the radiative/convective models within a factor of 2 or so. The real climate system contains many feedback effects, as in snow/ice albedo, cloud properties, and mixing of heat with the deep ocean layers. With our present ignorance of these effects, we are forced to assume that the simple models yield appropriate order-of-magnitude estimates of temperature effects.

Under certain circumstances, for example in highly polluted regions, a trend in the surface irradiance or visibility might be measurable. For the same situation, a study of temperature fluctuations may be too noisy for establishing a cause and effect case against a specific pollutant (e.g., Husar et al. 1979). In this case, it may be necessary to resort to model analysis for a solution; however, the optical parameters for the pollutant must be known. Clearly, this approach is severe in terms of complexity and expense, and should be avoided unless there is ample justification for an undertaking. Generally, these situations are unique because of local topological conditions, so special consultation might be required for an investigation.

3. GASES AND SECONDARY PRODUCTS

A primary pollutant is defined as a substance that is directly released to the atmosphere. Secondary products are defined as transformed primary pollutants which may be in a gaseous

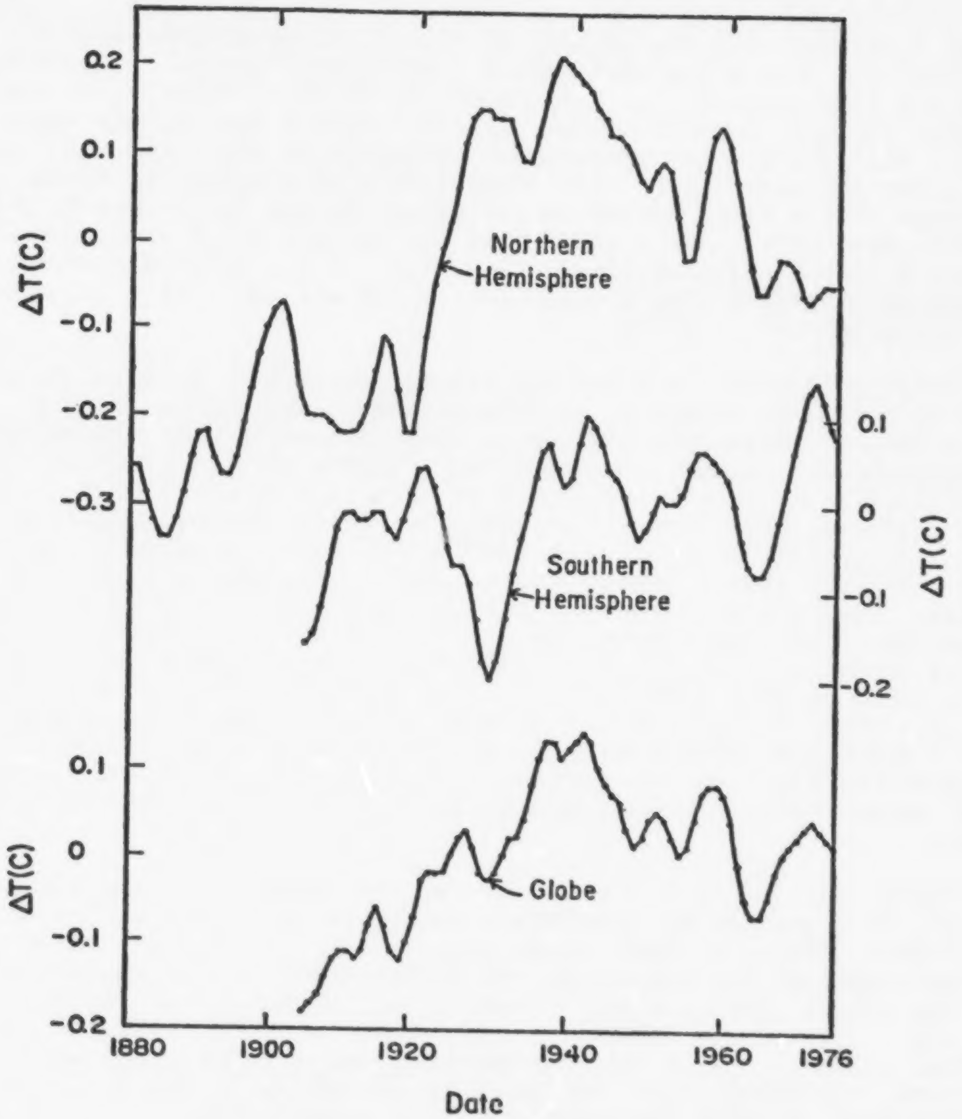


Figure 1. Global and hemispheric variations of surface air temperature during the past century, based on data for surface stations archived by the National Climate Data Center. (Graph supplied by panel member J. Hansen.)

or particulate form. The potential radiative effects will depend upon the five factors stated in the introduction.

For gases the most common case requiring examination will be absorption bands in the thermal infrared window region (8-14 μm). For this case an upper limit of the possible temperature change can be obtained simply from the total absorptance of the infrared bands. The thermal impact depends upon the location of the absorption in the window region, with bands in the most transparent regions having the largest effect. An estimate of the impact of an infrared absorbing gas on the surface temperature can be obtained from the relation

$$\Delta T = 0.18\ AB_{(\nu_o)}$$

where A is the band absorptance in inverse centimeters, i.e., the product of the band intensity and the vertical column amount of the absorbing gas, and $B(\nu_o)$ is the Planck flux ($W\ m^{-2}s^{-1}cm^{-1}$) at the frequency of the band center computed for a global mean surface temperature of 288 K. The gas amount can be found as the product of the projected gas release rate and its estimated lifetime. If ΔT found in this way is not negligible, e.g., if it is ≥ 0.1 K for a globally dispersed gas, then the gas should be examined in more detail. As a first step a more accurate estimate of the temperature impact could be obtained from a radiative/convective model.

Lifetime

One of the most powerful and reliable guides to estimating the potential importance of a substance is its lifetime in the atmosphere because it defines the time and space scales over which the substance will be distributed. The four factors listed below are quantities that can be used to estimate lifetimes.

(1) Reactivity with OH and other reactive substances (e.g., SO_2) in the atmosphere.
(2) Solubility in fresh and sea water.
(3) Absorption in biological surfaces and reaction characteristics on surfaces.
(4) Association with aerosols.

3.1. Reaction With Atmospheric Constituents

The lifetimes of pollutants can be controlled by reactions with one or more atmospheric constituents as indicated above. Also the transformation of one substance into another (generation of secondary pollutants) usually occurs by means of reaction with an atmospheric constituent. Information for establishing criteria could be obtained by testing for reactions with atmospheric constituents and identifying the reaction products. Ultimately, it may be necessary to understand the entire chain of atmospheric reactions, not merely the results of the first transformation.

3.2. Gas-Particle Transformations

If the primary pollutant undergoes transformations that lead to (1) new particle formation and (2) growth of existing particles, then clearly it will affect radiative transfer, and the composition of aerosols and precipitation (for which the particles act as CCN) may be altered. An assessment of such effects could be aided by testing the primary pollutant for (1) its ability to form particles under atmospheric conditions and for (2) its ability to cause a test aerosol to grow when subjected to atmospheric conditions.

4. PARTICLES

4.1. Direct Effects

Suspended particulate matter affects the radiation balance directly by scattering and absorbing both visible and infrared radiation. These optical effects have already led to visibility degradation (Husar et al. 1979) and a reduction in surface irradiance in urban areas (Ball and Robinson 1979; Peterson and Stoffel 1979) and may ultimately lead to regional and global climate modification. In order to understand and quantitate these effects, detailed knowledge of the optical properties of aerosol particles (i.e., absorption coefficient and angular distribution of scattering coefficient) as a function of particle size, chemical composition, and wavelength is necessary. Such detailed information is difficult to obtain, and it would not be appropriate from a cost benefit point of view to require such analyses. We, therefore, have considered an approximate three-parameter characterization of the aerosol optical properties to screen particulate emissions, which could have a significant impact on the radiation balance. Such a screening procedure would permit rapid processing of the vast majority of emissions which do not come close to being a radiative hazard. The three parameters that are relatively straightforward to measure are

(1) Submicron aerosol mass emission rate $\frac{dm_s}{dt}$,

where $m_s = \int_0^{r=1\mu} \frac{4\pi r^3}{3} N(r)\, dr$;

N(r) is the number distribution function, and r is particle radius.

(2) Integrated absorption coefficient per unit mass in the visible spectral region between 0.3 and 0.7 μ.

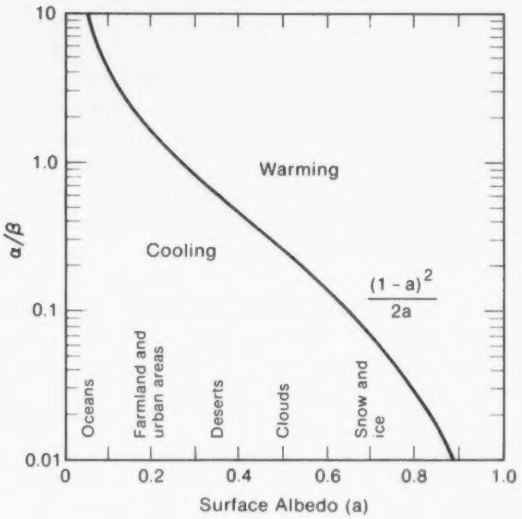


Figure 2. Warming and cooling of the atmosphere by aerosols as a function of the ratio of absorption (α) to backscattering (β) and the surface albedo (a) based on the results of Chylek and Coakley (1974).

(3) Integrated absorption coefficient per unit mass in the infrared window between 8 and 14 μ.

The optical properties of an aerosol are critical to the warming or cooling of the atmosphere. This is demonstrated in Figure 2 which shows warming or cooling of the atmosphere depending on the surface albedo and the absorption-to-backscatter ratio of aerosols.

Since the real part of the refractive index does not vary significantly from one substance to another (1.33 - 1.6), one can make an estimate of the scattering coefficient from the submicron mass alone (Bhardwaja et al. 1974). This estimate will be based on using the maximum scattering coefficient per unit mass, which is found for particles ≃ 0.1 - 0.4 μ in radius, and will therefore give an upper limit on the scattering contribution. The choice of particle density and size distribution is left open at this time; however, on the basis of experience a density of 2 g cm^{-2} and size distribution exponent of v=3 (based upon the Junge law $d N/d \log r \; \alpha \; r^{-v}$) would seem reasonable for calculation of a mass scattering coefficient until representative size distributions are made available. The other two parameters will give a direct measure of the absorption coefficient in the visible and infrared regions. These three parameters, when coupled to appropriate dispersion models, should allow an approximate estimate of the radiative temperature impact of these emissions on a local and regional basis. As a rule of thumb, if these emissions do not make a significant contribution to the ambient submicron mass, they will not make a significant perturbation on the scattering effects of particulates. The situation could be somewhat complicated by the absorption effects since a very small amount of highly absorbing material may produce large optical effects. This is demonstrated by the fact that "graphitic" carbon dominates the optical absorption coefficient in urban areas and industrial regions, yet it represents a relatively small fraction of the aerosol mass (Rosen et al. 1978 a and b, and Weiss et al. 1979). On the other hand, the likelihood of large releases of highly absorbing particles is seen as rather remote.

It is not possible to make a reliable estimate of the direct effect of aerosols on the radiation balance, or the indirect effects of gases or aerosols through modification of cloud properties, at our present state of knowledge. However, we can identify extreme cases that are likely to perturb the radiation balance. In the case of a purely absorbing aerosol, the optical thickness required to cause a warming of ~0.1K is ~0.002. Thus with the magnitude of a significant temperature perturbation defined as above, the limit on optical thickness for absorbing aerosols is given by

$$\Delta\tau_a \sim 0.02\ \Delta T,$$

with ΔT in °C. For a purely scattering aerosol the relation is

$$\Delta\tau_s \sim -0.09\ \Delta T$$

with increased aerosol loading causing a cooling effect in this case. These approximate relations are based on the assumption that the aerosol radiative effects in the visible are larger than in the thermal infrared, which is normally the case for aerosols small enough to remain airborne for a climatologically significant time. The optical thickness of the aerosols is given by

$$\tau = \int_0^\infty Q_{ext}(r)\ \pi r^2\ n(r)dr$$

where $n(r)dr$ is the number of particles above unit area with radius between r and $r + dr$, and $Q_{ext}(r)$ is the extinction efficiency factor (van de Hulst 1957; Hansen and Travis 1974); as an approximate upper limit Q_{ext} can be set equal to 2. Reliable size distribution measurements are important for the estimation of τ. If the temperature impact estimated in this way is found to be significant (as defined above) for a projected aerosol release, it should be subjected to more detailed study.

Gas and aerosol chemical releases may also indirectly impact the earth's radiation balance by modifying cloud properties. However, the physics involved is not adequately understood, and it is thus not possible to specify what gas or aerosol releases would be sufficient to cause a significant problem through radiative effects of cloud changes. Research in cloud and aerosol physics and the interactions with radiation must be pursued extensively before it will be possible to recommend constraints on gas and aerosol releases because of their potential effects on cloud properties. More will be said on this subject in Section 5.

With the exception of stratospheric particles, the lifetime of suspended particles in the troposphere is usually on the order of a few days to a few weeks at most. This does not completely void the possibility of subtle global radiative effects from gases that eventually end in the chemical makeup of clouds after long-range transport.

Chemicals released to the atmosphere are unlikely to react (if they do at all) with natural aerosols (ocean salts, crustal materials and biotic effluent) to produce any serious imbalance. If reactions should occur, then in all likelihood, larger particles may result and removal will occur sooner.

4.2. Indirect Effects

Aside from the effects of particulate emissions on clouds (discussed in section 5.1), probably the most important indirect impact of these emissions could be due to their catalytic activity. It is well known that very small concentrations of appropriate catalysts (e.g., Fe^{3+}, Mn^{+4}, soot) can dramatically change reaction rates (see, e.g., Middleton and Kiang 1979; Chang et al. 1978). These catalytic agents could significantly enhance atmospheric gas-to-particle loading and have a large impact on radiation imbalance. A screening procedure must therefore be developed to assess the possible catalytic role of various particulate emissions in effecting the transformation processes of SO_2 to particulate sulfur, NO_x to particulate nitrogen, and hydrocarbon to particulate carbon.

A well-defined generally applicable procedure for such screening is not readily available, and at present each effluent will have to be assessed individually with the advice of experts in the field if significant amounts of emissions are expected.

5. THE EFFECT OF CHEMICALS ON THE OPTICAL PROPERTIES OF CLOUDS

Before dealing with the specifics of this problem, several general observations are worth noting. First of all, the interactions between atmospheric chemicals and the hydrologic cycle are not well understood, even in the case of ubiquitous quantities such as sulfur and nitrogen compounds. Consequently, one can hardly expect to make definitive statements with regard to the somewhat more esoteric compounds being produced by the chemical industry. Second, deducing the radiative effects of an absorbing particulate in an atmosphere containing clouds is not a trivial problem. Even answering the simplest possible problem, which is whether the particles are likely to warm or cool the environment, is complicated by many factors such as the index of refraction of the particles, the location of the particle layer, the optical properties of the clouds, and the albedo of the underlying surface. Finally, our understanding of the nature of gas-to-particle conversion in the atmosphere is still incomplete. This makes it difficult to predict with certainty whether or not released gases will become particles and, if they do so, what the chemical constituency of the particle would be.

These preliminary comments should not be construed as implying that no assessment of the effects of chemicals on clouds can be made. Rather, they are meant to convey some of the difficulties that must be faced in making these assessments. Since our knowledge of cloud formation systems is incomplete, any assessment is likely to contain some aspects that are based more on scientific speculation and educated estimates than on scientific facts. Additionally, there will be many cases in which a qualitative assessment can be made with some degree of certainty but where a quantitative assessment is out of the question.

Turning now to the specifics of the problem, there are two principal questions to be considered. The first, and perhaps the most important, is whether particulates, either primary or secondary, are likely to act as cloud condensation nuclei (CCN) and what effect these nuclei would have on the cloud droplet size distributions. The second is whether gases or particles will affect the radiative properties of the clouds directly. The effect of gases can be treated fairly simply but the particulates present a substantially more difficult problem.

5.1. The CCN Problem

An assessment of the effect of particulates as CCN can be made as follows:

(1) What is the size distribution of the particles?

For the particles to act as effective CCN, the particle radius must be in the general range $0.11 < r < 5.0$ microns. If the particles are smaller than this they are unable to attract water because of curvature effects. (Note the growth characteristics illustrated in the Kohler curves of Figure 3.) Larger particles tend to fall out of the atmosphere before they achieve significant concentrations.

(2) What is the solubility of the particles?

Chemical substances with low solubility are poor CCN since high water vapor supersaturations are required to make them grow.

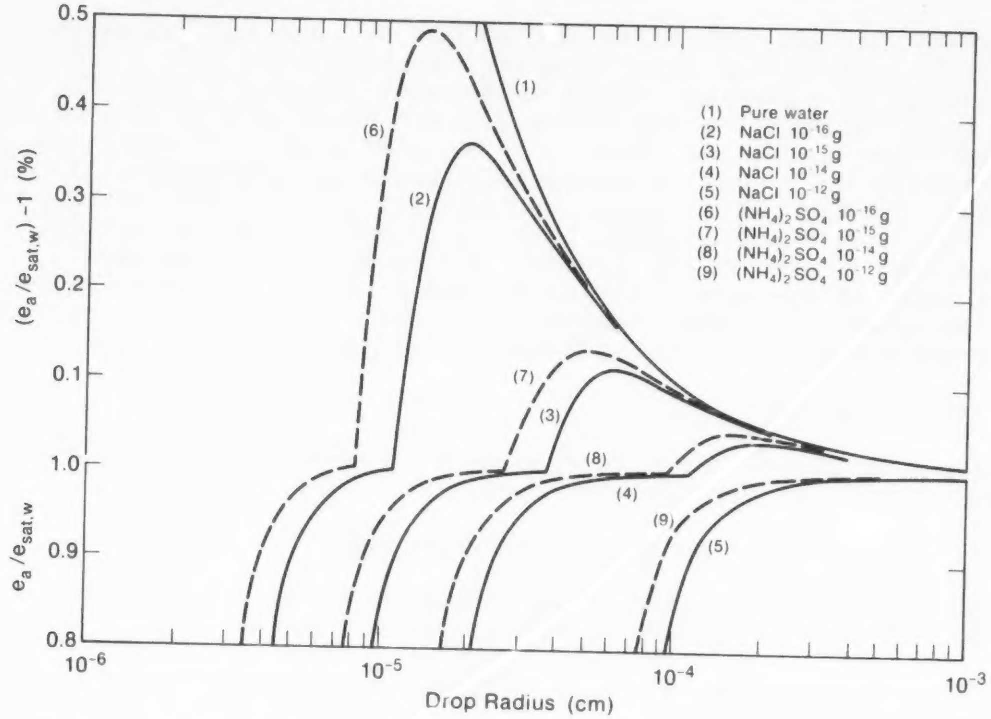


Figure 3. Variation of equilibrium vapor pressure over an aqueous solution drop with drop size, for various amounts of NaCl (solid lines) and $(NH_4)_2SO_4$ (dashed lines) in solution, and for 20°C (after Pruppacher and Klett 1978).

(Note the growth curves for pure water and weak solution droplets as opposed to those for strong solutions in the figure.) Conversely, hygroscopic substances such as salts and some acids (e.g., NaCl and H_2SO_4) are very effective CCN. Thus, if the chemical under study is a polymer or forms a particulate composed of organic compounds, it is unlikely to be important as a CCN. But if it is a sulfate or nitrate or reacts with such species, it may have a significant effect.

(3) What is the quantity of the added CCN relative to the ambient CCN?

If the number of additional CCN is less than 1% of the ambient CCN on the local or regional scale CCN are probably unimportant. This is not a rigid condition because a small number of hygroscopic CCN can cause a substantial change in the size distribution of a local cloud. (For an example see the study by Barrett et al. 1979.) Obviously a local effect must be evaluated in relation to surrounding regional effects.

(4) What are the radiative effects?

Given that the particles act as CCN and are sufficiently numerous to affect the cloud droplet distribution, their radiative effects must be assessed. This assessment cannot be made a priori since changes in the cloud droplet spectra will depend on both the composition and number of the particles. In addition, the particles will usually change the index of refraction of the droplets. Twomey (1977) suggests that for all but the thickest clouds (optical depth greater than 100), adding particles will increase the albedo of the system. Since his calculations neglect some of the complexities of the problem, his conclusions should be used with care. (Note: the basic logical chain of this and subsequent sections is outlined in Figure 4).

5.2. The Absorption Problem

As we mentioned above, the effect of gaseous absorption can be treated in a straightforward manner:

(1) What is the solubility of the gas?

Obviously, if the gas is not soluble, it will not have a large effect on the radiation balance of a cloud.

(2) What are the spectral absorption characteristics of the gas in solution?

Pure water droplets are non-absorbing at visible wavelengths but many solutions absorb radiation because of the properties of the solute. If the solution formed by the released gas is moderately or strongly absorbing, it can have a noticable effect on the heating in the cloud.

(3) What are the radiative effects?

Typical estimates of radiative cooling from stratus clouds are ~0.5 K per hour. Consequently, a heating rate of ~0.1 K per hour due to dissolved gases would be a significant addition to the radiation budget of stratus clouds. It is very unlikely that heating rates would reach the rates associated with cumulus clouds since these rates are an order of magnitude larger than those for stratus clouds.

Dealing with the effect of particulates on the absorption characteristics of a cloud is difficult because we know very little of what happens to the particulates in the cloud. While we can sketch a general approach, much of the quantitative knowledge needed is not yet available. Questions asked in the approach are as follows:

(1) Is the particulate soluble?

If the particulate is soluble, it acts as a CCN (see section 5.1). In general, it will also change the optical properties of

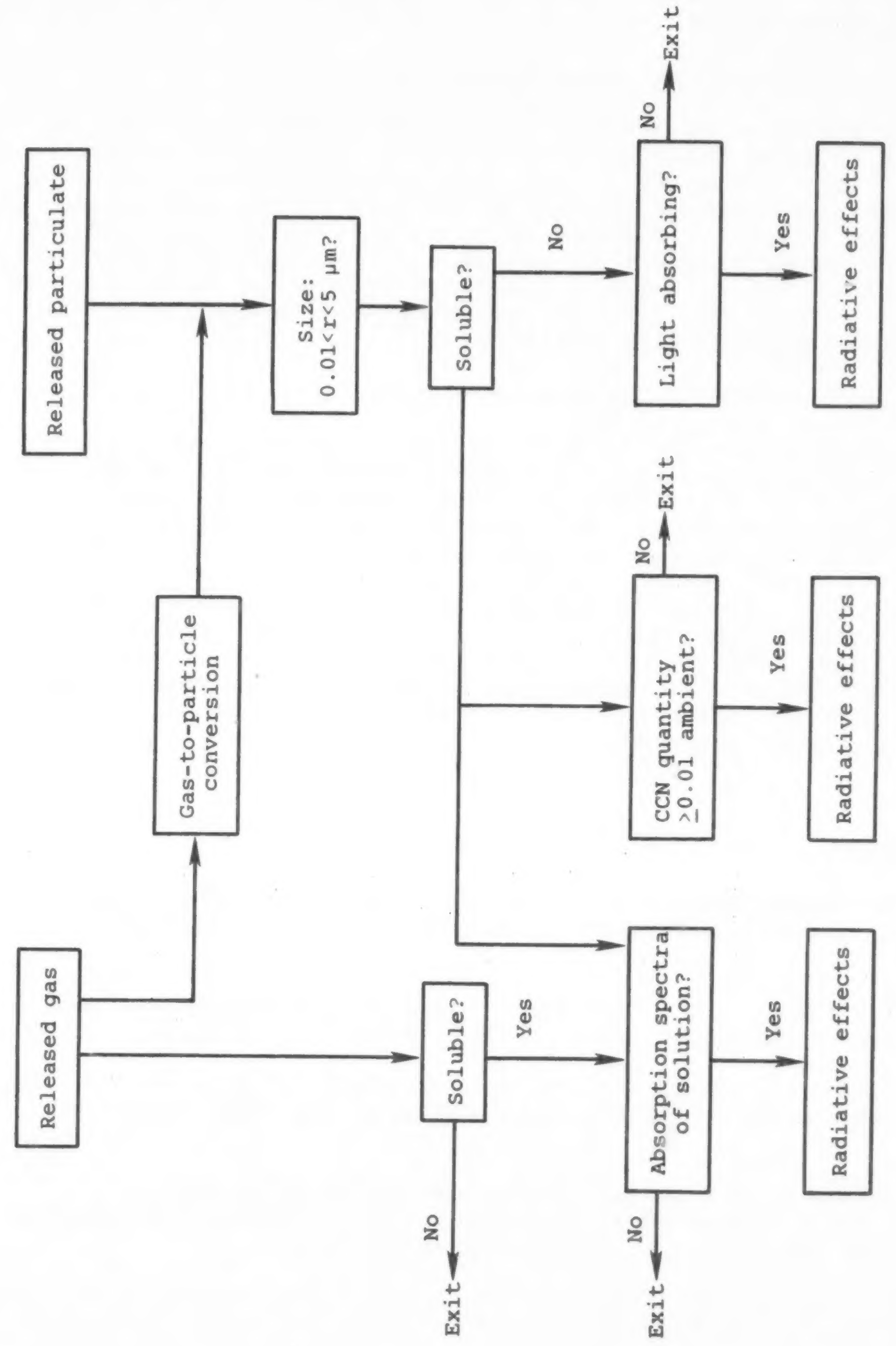

Released particulate
Released gas
Gas-to-particle conversion
Size: 0.01<r<5 μm?
Soluble?
No
Light absorbing?
No
Exit
Yes
Radiative effects
CCN quantity ≥0.01 ambient?
No
Exit
Yes
Radiative effects
Soluble?
Yes
No
Exit
Absorption spectra of solution?
Yes
Radiative effects
No
Exit

Figure 4. Flow diagram.

the cloud drops, and this effect should be handled as outlined in the procedure for gases.

(2) Is the particle light-absorbing?

If the particle is neither soluble nor light-absorbing, it is unlikely to have climatic implications. If it does absorb visible radiation, then it is potentially important as a modifier of the radiation field of the cloud. Because of the high number of scattering events in a cloud which usually is optically thick ($\tau_c > > 1.0$), a small quantity of material can absorb a significant amount of energy. The absorbing particle can exist then on the surface, within the droplet, or in the air between droplets and absorption effects will still occur.

(3) What are the radiative effects?

Some general answers to this question for nonsoluble particles have been proposed by Ackerman and Baker (1977). They conclude that pure scattering particles increase the system albedo for all types of clouds. Absorbing particles increase the albedo for thin clouds but decrease it for moderate to thick clouds. This latter effect is due to the dominance of absorption over backscatter effects as the optical depth increases. These results are only qualitative and need to be greatly extended before they could be used to assess the impact of absorbing particles of clouds. It would also be necessary to relate the magnitude of these effects to others that affect clouds on the local and regional scale.

6. REFERENCES

Ackerman TP, Baker MB. 1977. Shortwave radiative effects of unactivated aerosol particles in clouds. J. Appl. Meteorol. 16(1):63.

Atwater MC. 1975. Thermal changes induced by urbanization and pollutants. J. Appl. Meteorol. 14(6):1061.

Atwater MA. 1977. Urbanization and pollutant effects on the thermal structure in four climatic regimes. J. Appl. Meteorol. 16(9):888.

Ball RJ, Robinson GD. 1979. The origin of haze in central U.S.A. and its effects on solar irradiation. Center for Environment and Man, Hartford, CT, Rep. 4222-670, 74 pp.

Barrett EW, Parungo FP, Pueschel RF. 1979. Cloud modification by urban pollution: A physical demonstration. Meteorol. Rundsch. 32(5):136.

Bhardwaja PS, Herbert J, Charlson RJ. 1974. Refractive index of atmospheric particulate matter: An in situ method for determination. Appl. Opt. 13(4):731.

Butcher SS, Charlson RJ. 1972. An introduction to air chemistry. Academic, NY.

Chang SG, Brodzinsky R, Toosi R, Markowitz SS, Novakov T. 1979. Catalytic oxidation of SO_2 on aqueous suspensions. Conf. on Carbonaceous Particles in the Atmosphere, Mar. 20-22, 1978, Lawrence Berkeley Lab., Berkeley, CA, LBL-9037, pp. 122-130.

Chylek P, Coakley J. 1974. Aerosols and climate. Science 183:72-75.

Clarke JF. 1969. Nocturnal urban boundary layer over Cincinnati. Mon. Weather Rev. 97(8):582.

Hansen JA, Travis LD. 1974. Light scattering in planetary atmospheres. Space Sci. Rev. 16(4):527.

Husar RB, Paterson DE, Holloway JM. 1978. Trends of eastern U.S. haziness since 1948. Preprint Proc. 4th Symp. on Turbulence, Diffusion, and Air Pollution, Reno, Nev., Jan. 15-18, 1979, AMS, Boston, MA, pp. 249-256.

Manabe S, Wetherald RT. 1967. Thermal equilibrium of the atmosphere with a given distribution of relative humidity. J. Atmos. Sci. 24(3):241.

Middleton P, Kiang CS. 1979. Relative importance of nitrate and sulfate aerosol production mechanisms in an urban atmosphere. In: Grosjean D, ed. Nitrogenous air pollutants, chemical and biological implications. Ann Arbor Science Publishers Inc., Ann Arbor, MI, p. 269.

Peterson JT, Stoffel TL. 1979. Urban-rural solar radiation measurements in St. Louis, Missouri. NOAA Tech. Memo. ERL-ARL-76, 51 pp.

Pruppacher HR, Klett JD. 1978. Microphysics of clouds and precipitation. D. Reidel Publishing Co., Dordrecht, Holland; Boston, MA, 714 pp.

Ramanathan V, Coakley JA. 1978. Climate modeling through radiative-convective models. Rev. Geophys. Space Phys. 16(4):465.

Robinson GD. 1958. Some observations from aircraft of surface albedo and the absorption of clouds. Arch. Meteorol. Geophys. Bioklimatol., Ser. B,9:28-41.

Rosen H, Hansen ADA, Gundel L, Novakov T. 1978. Identification of the optically absorbing component in urban aerosols. Appl. Opt. 17(24):3859.

Rosen H, Hansen ADA, Gundel L, Novakov T. 1979. Identification of the graphitic carbon component of source and ambient particulates by Raman spectroscopy and an optical attenuation technique. Proc. Conf. on Carbonaceous Particles in the Atmosphere, Mar. 20-22, 1978, Lawrence Berkeley Lab, Berkeley, CA, LBL-9037, pp. 49-55.

SCEP. 1970. Man's impact on the global environment: assessment and recommendations for action. Report on the Study of Critical Environmental Problems. Massachusetts Institute of Technology Press, Cambridge, MA, 319 pp.

Twomey S. 1977. The role of aerosols in influencing radiative properties of clouds. In: Bolla HJ, ed. Symposium on radiation in the atmosphere, IAMAP, Garmisch-Partenkirchen, Germany, August 19-28, 1976, Science Press, Princeton, NJ, pp. 171-175.

Twomey S. 1977. The influence of pollution on the shortwave albedo of clouds. J. Atmos. Sci. 34(7):1149-1152.

van de Hulst HC. 1957. Light scattering by small particles. John Wiley and Sons, New York, NY, 470 pp.

Wang WC, Yung YL, Lacis AA, Mo T, Hansen JE. 1978. Greenhouse effects due to man-made perturbations of trace gases. Science 194(4266):685-690.

Weiss RE, Waggoner AP, Charlson RN, Thorsell DL, Hall JS, Riley LA. 1979. Studies of the optical, physical and chemical properties of light absorbing aerosols. Proc. Conf. on Carbonaceous Particles in the Atmosphere, Mar. 20-22, 1978, Lawrence Berkeley Lab., Berkeley, CA, LBL-9037, pp. 257-262.

APPENDIX: Atmospheric Chemical Processes

The material below is quoted from Atmospheric Chemistry, Problems and Scope, NAS, Washington D.C., 1975, pp. 108-109:

The Role of Aerosol

Figure [A-1] shows the atmosphere as a chemical system with a flow of trace substances from source to sink via a large number of possible routes. Various classes of trace substances or their physical state are shown as separate boxes in the diagram.

These figures show two basic types of meteorological effect resulting from the presence of specific trace substances in the atmosphere: (1) direct radiative interactions and (2) water in nucleation processes and the like. Nucleation processes are manifested in two general ways:

(1) Modification of albedo by changes in clouds, or other changes in radiative processes, including modification of surface albedo by snow accumulation, conversion to desert, and dry soil to wet soil;
(2) Hydrometeor modification, including amounts, composition, and optical properties.

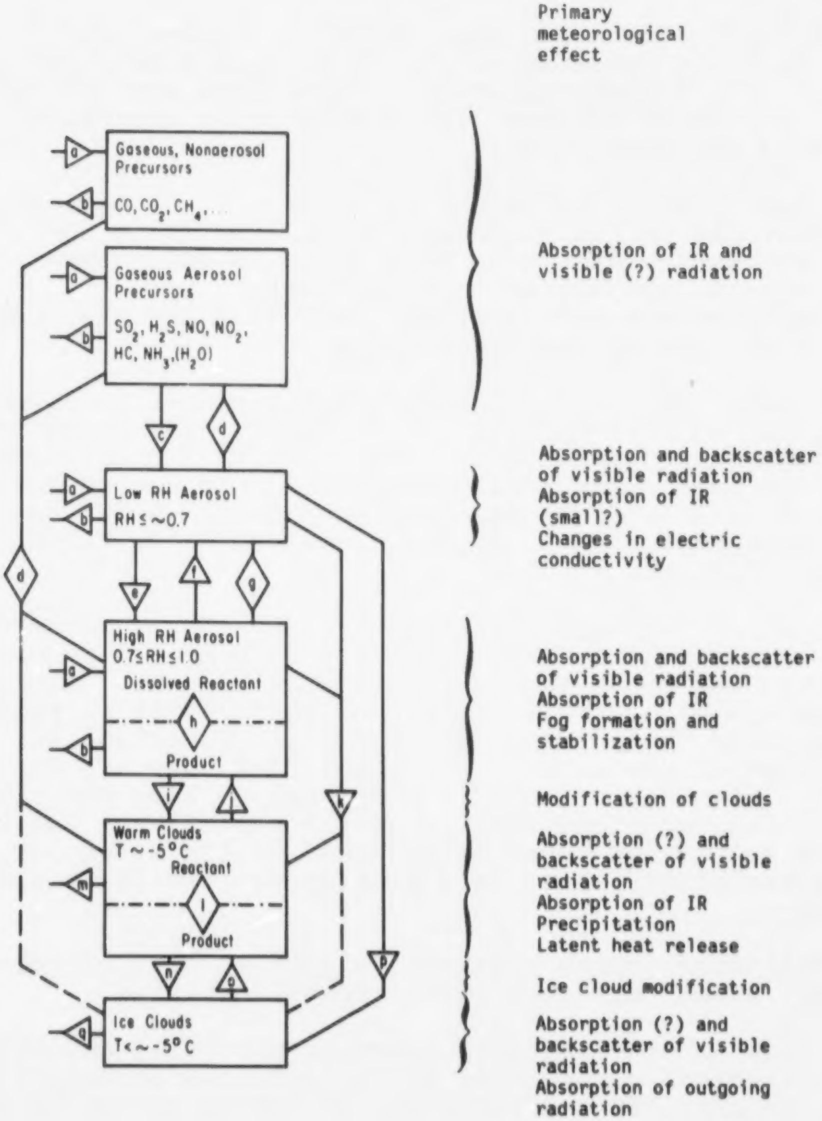
It is clear that most current efforts center on direct climatological involvement via albedo changes and modification of other radiative processes (SCEP 1970). While a great deal of attention has been given to the study of cloud and nucleation microphysics, little of it has developed to the point at which global or even mesoscale or synoptic-scale effects can be unequivocally explained.

There still are uncertainties about whether increases in atmospheric particulate matter will act to heat or to cool the earth. The uncertainty exists for several reasons. First, there are various approaches to ascertaining the effects of particulate matter even when the physical and chemical properties are known. Unfortunately, in the case of the atmosphere they are not known well enough. It is particularly important to know the sizes, shapes, and indices of refraction of the particles. The complex part of the refractive index is governed by the molecular character of the particles, which is a problem of certain interest to air chemistry.

The following topics represent a partial list of relevant problems for which increased effort seems justified.

(1) Rate of conversion of gases to particles and the climatological consequence of the aerosols so created;
(2) The possible stabilization of fog or clouds by organic matter;

(3) The role of deliquescence in radiative balance of clouds, fog, and haze;
(4) Relative importance of reactions in cloud drops to gas phase reactions in 1;
(5) Role of nucleation (both cloud condensation nuclei (CCN), and ice nuclei (IN) in changing albedo of clouds;
Role of CCN and IN in changing area covered by clouds or cloud height.


Primary meteorological effect
Gaseous, Nonaerosol Precursors
CO, CO_2, CH_4, ...
Gaseous Aerosol Precursors
SO_2, H_2S, NO, NO_2, HC, NH_3, (H_2O)
Absorption of IR and visible (?) radiation
Low RH Aerosol
RH ≤ ~0.7
Absorption and backscatter of visible radiation
Absorption of IR (small?)
Changes in electric conductivity
High RH Aerosol
0.7 ≤ RH ≤ 1.0
Dissolved Reactant
Product
Absorption and backscatter of visible radiation
Absorption of IR
Fog formation and stabilization
Modification of clouds
Warm Clouds
T ~ -5°C
Reactant
Product
Absorption (?) and backscatter of visible radiation
Absorption of IR
Precipitation
Latent heat release
Ice cloud modification
Ice Clouds
T < ~ -5°C
Absorption (?) and backscatter of visible radiation
Absorption of outgoing radiation
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q

←

Figure A-1. The troposphere as a chemical system. Rectangles are recognizable entities in the atmosphere. Triangles represent processes that have a single direction of material flow, and diamonds (two triangles) represent reversible processes. a, Sources; b, sinks; c, gas-to-particle conversion; d, sorption; e, deliquescence; f, efflorescence; g, Raoult's equilibrium; h, reaction in concentrated solution droplet; i, nucleation and condensation of water; j, evaporation; k, capture of aerosol by cloud drops; l, reaction in dilute solution; m, rain; n, freezing of supercooled drop by ice nucleus; q, precipitation. (Butcher and Charlson 1972, p.8, with permission of the authors and the copyright holder, Academic Press; primary meteorological effects were added for publication in Atmospheric Chemistry: Problems and Scope, National Academy of Sciences Panel on Atmospheric Chemistry, Washington, DC, 1975.)

Report of a Workshop on
ANTHROPOGENIC CHEMICALS AS MODIFIERS OF CLOUDS AND PRECIPITATION

Boulder, Colorado
September 1979

Edited by
Earl W. Barrett

Preceding page blank

PARTICIPANTS AND CONTRIBUTORS

Dr. Earl W. Barrett
NOAA-ERL-APCL, R31
Boulder, CO 80303
(303) 497-6260
(FTS 320-6260)

Dr. Barry A. Bodhaine
NOAA-ERL-GMCC, R329
Boulder, CO 80303
(303) 497-6659
(FTS 320-6659)

Dr. Richard D. Cadle
National Center for
Atmospheric Research
Boulder, CO 80303
(303) 494-5151

Dr. William G. Finnegan
Dept. of Atmospheric Science
Colorado State University
Fort Collins, CO 80523
(303) 491-8667 or -8257

Dr. Norihiko Fukuta
Dept. of Meteorology
University of Utah
Salt Lake City, Utah 84108
(801) 581-6136

Dr. Edward E. Hindman
Dept. of Atmospheric Science
Colorado State University
Fort Collins, CO 80523
(303) 491-8511 or -8675

Dr. Wallace E. Howell
U.S. Bureau of Reclamation
P.O. Box 25007
Denver, CO 80225
(303) 234-3384
(FTS 234-3384)

Dr. John A. Kadlecek
Atmospheric Sciences Research
Center
State University of New York
at Albany
1400 Washington Ave.
Albany, NY 12222
(518) 457-4930

Dr. John M. Miller
NOAA Air Resources Labs.
8060 13th St.
Silver Spring, MD 20902
(301) 427-7645

Dr. Farn P. Parungo
NOAA-ERL-APCL, R31
Boulder, CO 80303
(303) 497-6460
(FTS 320-6460)

Dr. Russell C. Schnell
NOAA-ERL-APCL, R31
Boulder, CO 80303
(303) 497-6822
(FTS 320-6822)

Charles Van Valin
NOAA-ERL-APCL, R31
Boulder, CO 80303
(303) 497-6279
(FTS 320-6279)

Dr. Helmut K. Weickmann
CIRES, PSRB #3
3100 Marine St.
Boulder, CO 80302
(303) 497-6289
(FTS 320-6289)

CONTENTS

Page

PARTICIPANTS AND CONTRIBUTORS 192

PREFACE 194

1. HOW DO CLOUDS FORM AND PRODUCE PRECIPITATION? 195

2. HOW CAN CHEMICALS AFFECT THESE PROCESSES? 198

3. EFFECTIVENESS OF CHEMICALS AS NUCLEI 201

4. BACKGROUND NUCLEUS CONCENTRATIONS: SOME QUANTITATIVE CONSIDERATIONS 204

5. SENSITIVITY OF PRECIPITATION TO VARIATION IN NUCLEUS CONCENTRATIONS 207

6. CONCLUSIONS AND RECOMMENDATIONS 216

7. TECHNIQUES FOR TESTING NUCLEATION EFFICIENCY 218

8. ACKNOWLEDGMENTS 224

9. REFERENCES 224

PREFACE

This workshop was sponsored by the Office of Toxic Substances of the Environmental Protection Agency and held at the Boulder Environmental Research Laboratories of the Department of Commerce, Boulder, Colorado on 24-25 September 1979. The workshop panel consisted of eleven full-time and three part-time participants with expertise in atmospheric chemistry, nucleation physics and chemistry, aerosol physics and chemistry, and weather modification theory and practice.

The charge given to the panel was (1) to evaluate the possibility of significant environmental impact of chemical substances on precipitation patterns by virtue of their influence on the cloud-microphysical processes that produce precipitation, and (2) to recommend laboratory test procedures for screening chemicals in case such impacts are identified. Other environmental impacts that could conceivably arise from the interactions of chemicals with clouds, such as changes in pH of precipitation or changes in the Earth's radiation balance by alteration of the reflectances of clouds, were not treated by the panel.

ANTHROPOGENIC CHEMICALS AS MODIFIERS OF CLOUDS AND PRECIPITATION

1. HOW DO CLOUDS FORM AND PRODUCE PRECIPITATION?

A brief discussion of the processes leading to precipitation is helpful in understanding how anthropogenic chemicals might influence these processes. The reader who is interested in a more complete treatment is referred to any of the standard texts on cloud physics, such as Mason (1971), Byers (1965), or Fletcher (1962).

Clouds are formed by cooling of moist air. Either, or both, of two cooling mechanisms may be involved, viz., radiative cooling or cooling by expansion when air ascends from high pressure to low. The first is effective in generating fogs near the ground and stratiform clouds aloft; the second is dominant in convective cumuliform clouds. Generally speaking, clouds that produce significant amounts of precipitation are formed by expansion in updrafts. Because the equilibrium, or saturation, vapor pressure of water decreases strongly with temperature, the relative humidity of the cooling volumes of air increases as the temperature falls, and eventually reaches saturation (100%).

Everyday experience might lead one to believe that water should condense into drops when saturation is reached. This, however, is not necessarily the case in the free air away from solid surfaces. In perfectly clean air containing no solid or liquid particles, droplets will not begin to form until the relative humidity rises to about 400% (300% supersaturation). At this point, condensation will take place on ions created by cosmic rays or terrestrial radioactivity. This is the basis of a variety of "cloud chambers" that are used in the study of nuclear particles. In order for drops to form at relative humidities near 100%, the air must contain small solid or liquid particles that can serve as cloud condensation nuclei (CCN). Other factors being equal, the larger the airborne particle the more effective it will be as a CCN. (The effectiveness of a particle as a CCN is expressed in terms of the relative humidity --or supersaturation--that the air must reach in order to grow a drop on that particle.) On the other hand, the larger the particle the faster it will settle out of the atmosphere. As a result, CCN in the atmosphere consist of particles with diameters in the range 0.01 micrometer (μm) to several μm. Particles smaller than that require supersaturation of several or even tens of percent to work as nuclei and therefore are not considered to be effective CCN.

The number-vs.-size spectrum, or size distribution, of droplets in a young cloud is therefore determined by the size distribution of the available particles, the total concentration (number per unit volume of air) of particles, and the physical and chemical properties of the particles that determine their nucleating effectiveness. The theory of nucleation of cloud droplets by pure soluble substances is well-developed; it is discussed in section 3.

Once the droplets have condensed on a nucleus they continue to grow by condensation of vapor that diffuses to the drop. It is characteristic of diffusional growth that the initial rate of increase of drop radius is rapid, but decreases as the drop gets larger. Under steady-state conditions the drop diameter is proportional to the square root of elapsed time. This means that drops that are nucleated later in time tend to catch up in size with those nucleated earlier, thereby giving rise to a rather narrow droplet-size distribution in the cloud. The actual drop growth rate is proportional to the supersaturation, which in turn tends to be proportional to the cooling rate and therefore (usually) to the updraft speed. In many cases the growth rate is so slow that the droplets cannot grow big enough to fall through the updraft and are carried out of the cloud top into drier air where they evaporate. This is why many small cumulus clouds, or shallow stratus clouds, never produce precipitation.

A typical droplet in a young cloud has a diameter of order 10 μm, whereas an average raindrop has a diameter of order 1 mm. Assuming that the conditions in a cloud are such that a newly-nucleated droplet grows to 5 μm diameter in the first second after nucleation, the time required for the same drop to reach a diameter of 1 mm by diffusional growth would be 11.1 h. This is longer than the lifetime of most clouds and greater than the depth of the clouds divided by the mean updraft speed. Other mechanisms must therefore exist to account for the much speedier onset of precipitation.

Looked at in another way, the volume of an average raindrop is roughly equal to that of 1 million average cloud droplets. If a cloud is to generate rain in a reasonable time, it is necessary that this many cloud droplets aggregate to form the raindrop. That is possible only if the distribution of droplet diameters is broad enough so that the fall speed of larger droplets relative to the updraft is significantly greater than that of the smaller ones. The larger droplets collide with smaller ones; in a significant fraction of these collisions the smaller merge with the larger. The added mass increases the fall speed of the large drop, thereby increasing the collision frequency, etc. This gives rise to an avalanche process that can grow raindrops provided that the cloud is deep enough and contains sufficient total liquid water and an adequate vapor supply. Many clouds do not meet the requirements and so do not precipitate at all.

The mechanism of raindrop formation outlined above is known as the collision-coalescence process, or, more commonly, the coalescence process. There is another mechanism that operates to produce precipitation-size particles in a short time in clouds that extend to altitudes above the 0°C isotherm. This process depends on the existence of an energy barrier to the freezing of pure *liquid* water that is analogous to the barrier that impedes the condensation of pure water *vapor* unless a nucleus is available. Water droplets cannot freeze unless they contain or come into contact with a suitable solid body or unless the temperature is below about -40°C.

In middle and high latitudes, most clouds are deep enough that their tops are colder than 0°C; cumulonimbus clouds that produce severe thunderstorms and tornadoes have top temperatures of -60°C or colder. The middle and upper parts of young, growing, middle- and high-latitude clouds therefore consist mainly of small supercooled droplets. These can freeze only if they contain or come into contact with an effective *ice nucleus* (IN). The effectiveness of an IN is expressed in terms of the temperature at which it causes a drop to freeze or nucleates an ice crystal directly from the vapor phase; the warmer the nucleation threshold the higher the effectiveness. Natural IN have activation temperatures ranging from -1°C to -30°C or lower, but very few natural airborne IN are active at temperatures warmer than -10°C.

In a supercooled cloud the prevailing humidity is close to water saturation at the existing temperature. Because the saturation vapor pressure over water is always greater than that over ice at temperatures below 0°C, a newly-frozen droplet or embryonic ice crystal finds itself in a much more supersaturated environment than that of the unfrozen droplets. The diffusional growth of the ice crystals will therefore be very rapid; even with the $(\text{time})^{1/2}$ dependence of the particle diameters the ice crystals will grow to precipitation size in a minute or less. The crystals grow at the expense of the unfrozen drops; the latter evaporate some of their water to feed the growing crystals if the humidity drops below water saturation. The crystals will fall through the cloud and reach the ground as snow if the temperature at the ground is colder than 0°C; otherwise they will melt and fall as rain. This mechanism of precipitation production is known as the *ice-crystal process*, or the *Bergeron-Findeisen* process (after the two meteorologists who first proposed it).

The coalescence process operates alone only in clouds that are (1) warmer than 0°C throughout, and (2) deep enough for the process to be efficient. These conditions are met only in tropical clouds and in subtropical clouds in summer. The process does, however, play a role in initiating precipitation in summer mid-latitude clouds in the United States (Battan 1953, Braham 1957, Changnon et al. 1977). Likewise, the ice-crystal process operates alone only in relatively thin clouds at temperatures below 0°C. In clouds with high concentrations of snow crystals, *aggregation* of these into larger snowflakes by collision and sticking acts to form larger snowflakes. Also, crystals can sweep up supercooled droplets in their fall; these freeze on contact with the crystal and increase its mass. This accretion or riming process leads to quick formation of large ice particles and raindrops and, in strong updrafts, to hailstones.

A special case of the ice-crystal process is found frequently in the warm-frontal portions of low-pressure storm systems, especially in temperate-maritime climates such as the Pacific Northwest and western Europe. In these systems, two (or more) stratiform cloud decks separated by a layer of clear air are frequently found. The upper layer, or "releaser" cloud is cold, possibly near -40°C at the top, and hence is well-glaciated but contains only a small mass concentration of water-substance because of the low temperature. The lower deck is warmer and so contains much liquid water in the form of small supercooled drops, but these would not normally freeze because of a lack of IN active at the in-cloud temperature (-10°C to -15°C, for example). Ice crystals that fall from the upper deck enter the lower "spender" cloud and serve as 100% effective IN for that cloud, thereby releasing the water in it faster and ultimately in greater amount than would have occurred in the absence of the releaser cloud. The same thing happens when convective (cumulus) clouds grow inside a pre-existing stratiform cloud deck containing much ice; the cumuli are seeded much more effectively than if they had developed in clear air (Hall 1957).

From the foregoing it should be clear that: (1) only those clouds that are sufficiently deep and have long enough lifetimes (or strong enough updrafts) will produce precipitation; and (2) that atmospheric particulate matter with diameters in the range 0.01 μm to a few μm is intimately involved in the mechanisms of precipitation production.

2. HOW CAN CHEMICALS AFFECT THESE PROCESSES?

Chemicals introduced into the atmosphere can alter the rate of precipitation in three basic ways.

(1) They may act as effective CCN or IN or both.
(2) They may "poison" nuclei that are already present in either of two ways:
    (a) They may coat dry nuclei with a hydrophobic (water-repellent) or passivating layer, or
    (b) They may dissolve in droplets and react with potential IN so as to reduce or destroy their effectiveness.
(3) They may dissolve in supercooled droplets endothermically, thereby chilling them so that they freeze spontaneously. Such substances can be called "pseudo-IN."

It is now necessary to consider the possible effects of addition (or removal) of nuclei on the clouds and on the precipitation mechanisms. In all cases the effects depend on the population of nuclei present prior to introduction of an anthropogenic substance. CCN, for example, vary widely in size distribution and chemical composition, depending on geography and proximity to more or less steady natural or artificial sources. CCN counts in tropospheric air above the boundary layer range from less than 1/cm^3 to 100/cm^3 or so, with most of the particles being found in the small size range with diameters less than 0.2 µm. In the boundary layer over the oceans, the number of smaller particles is about the same but the number of large (diameters from 0.2 to 2 µm) and giant (diameters greater than 2 µm) particles increases, especially when the sea is rough and whitecaps are present (Byers 1965, ch. 5; Allee et al. 1976). In urban areas the concentrations and size spectra vary widely depending on the automotive and industrial emissions. Typical concentrations are of the order of 1,000/cm^3 in the St. Louis area (Auer 1975, Fitzgerald and Spyers-Duran 1973) and 2,000-3,000/cm^3 in Los Angeles as estimated from particle size-distribution measurements (Barrett et al. 1979). With the exception of the Los Angeles data, the numbers are for CCN active at about 1% supersaturation; the number active at typical cloud supersaturations of the order of 0.1% is undoubtedly lower.

Maritime clouds form on a CCN population that is lower in number concentration but broader in size distribution than continental or urban clouds. The maritime clouds therefore tend to have fewer droplets per unit volume but a broader initial size distribution. They are characterized by higher coalescence efficiency and would therefore start to precipitate earlier than continental clouds, other factors being equal. Addition of anthropogenic CCN composed mainly of small particles to the maritime boundary layer will render the clouds more continental in character (more droplets with narrower size distribution) and so delay the onset of rain insofar as this onset is determined by the coalescence process. Addition of anthropogenic large and giant CCN, on the other hand, will cause clouds to become more maritime in character and speed up the start of rain. This has, in fact, been observed in Los Angeles (Barrett et al. 1979). Unpolluted stratocumulus clouds over the sea had droplet spectra that were heavily skewed toward large sizes; the nuclei were mostly sea-salt particles. Clouds nucleated by the urban smog (containing most small sulfate particles) had narrower spectra and were dominated by small drops. Clouds nucleated by a mixture of smog and oil-refinery effluent containing both small sulfate particles and large and giant nitrate and sulfate particles had droplet size spectra that were intermediate between the other two extremes. All three sets of clouds had about the same liquid-water content (0.1 g/m^3) and depth (~300 m). Similar effects have been reported by Hindman et al. (1976) and Braham and Dungey (1976) for clouds polluted by urban and industrial aerosols.

Although these measurements have shown clearly that modulation of the CCN concentration and particle size distribution does affect the droplet size spectra and therefore the colloidal stabilities of clouds, it is not at all clear if the amount of precipitation that falls from polluted clouds differs significantly from the amount that falls from "natural" clouds. Some observations (e.g., Warner 1968, Ramana Rao and Ramana Murty 1973) of rainfall up- and downwind of artificial CCN sources (burning sugar-cane fields and steel mills, respectively) seem to show decreases of rainfall downwind. On the other hand, the results of the METROMEX project at St. Louis do not show any clear-cut influence of CCN from urban pollution (Ackerman et al. 1978) except that radar echoes (showing the presence of precipitation-size drops) first appeared at levels between 600 and 1,100 m closer to the cloud base in the polluted clouds. Rainfall measurements downwind (east) of St. Louis were found to be generally higher than those upwind, but factors other than CCN, such as heat and moisture input from the city, are undoubtedly involved in causing the downwind excess; it cannot be ascribed solely to the added CCN.

On the basis of the evidence to date, it may be concluded that addition of artificial CCN to the atmosphere does not have significant impact on precipitation amounts in the middle and high latitudes, although strong, concentrated local CCN sources might produce local anomalies.

The clouds of major storm systems in middle and high latitudes (which provide most of the annual precipitation totals) are cold enough so that the ice-crystal process is dominant in producing precipitation. These clouds should be more susceptible to modification by increasing or decreasing the IN concentration, particularly IN that are effective at warmer temperatures. If a cloud or cloud system is deficient in IN, then introducing artificial IN will convert more of the small droplets into large ice crystals and thereby speed up the formation of precipitation. This is the basis of intentional precipitation-enhancement projects or experiments. Unfortunately, the total amount of precipitation that ultimately falls out of the clouds is affected by a large number of other physical factors and is not a simple function of the IN concentration. If, for example, a great excess of IN is introduced into a cloud, a large number of ice crystals will form and compete for the available water. The supersaturation with respect to ice will drop to a low value and the crystals will remain small. In this case, one would expect the onset of precipitation to be delayed and the total amount to be decreased. It might be expected, then, that there should exist an optimum IN concentration that would maximize precipitation from a particular cloud system. This optimum would, however, vary from one cloud system to another, and cannot be predicted with any degree of confidence at the present state of knowledge.

Real clouds are much more complex than the simple models that are used to describe them. As an example, an attempt was made by Weickmann (1974) to delay the onset of snowfall from stratocumulus clouds over the Great Lakes in order to reduce the heavy snowfalls in shoreline cities such as Buffalo, New York, and to deposit more of the snow farther inland. The procedure used was to "overseed" with artificial IN. One expected result was obtained: the snow crystals in unseeded portions of the cloud systems were large and heavily rimed with frozen cloud droplets and fell rapidly. On the other hand, the crystals in the seeded volumes were initially small and unrimed, as predicted. Unfortunately for the experiment, however, these small crystals were present in such large numbers that they aggregated very rapidly into large snowflakes that fell out just as soon as those from the unseeded cloud volume.

Chemicals that are hydrophobic may coat or be absorbed on existing nuclei and lower their effectiveness or make them totally inactive. In the case of CCN, reducing their numbers should give rise to clouds with greater percentage of large droplets and a higher coalescence efficiency. On the other hand, natural IN are often in short supply, so poisoning of IN would tend to inhibit precipitation by cold clouds.

IN that are already present in cloud drops can also be poisoned by chemicals that dissolve in the drops and react with the IN.

3. EFFECTIVENESS OF CHEMICALS AS NUCLEI

In order to act as a nucleus of either type, a substance must be dispersed into the atmosphere as a solid or liquid aerosol with particle diameters in the approximate range 0.01 to 2 μm, or as a gas that is subsequently converted to an aerosol by reaction with atmospheric constituents. *Any substance for which this is not the case can be eliminated as a possible precipitation modifier*.

A substance must be hydrophilic to act as an efficient nucleus of either type. *Any hydrophobic substance can be eliminated as a nucleus but may act as a nucleus poison*.

The theory of condensation nucleation by soluble aerosols of a single chemical species is well-developed and can be found in the cloud-physics textbooks referenced at the beginning of this report. The equation for the humidity required for equilibrium between a solution droplet and the air may be written as

$$\ln S = m_w \frac{2\sigma}{\rho R T r} - \frac{n \phi f}{1000} \qquad (3\text{-}1)$$

where S is the saturation ratio (relative humidity expressed as a fraction) at equilibrium, m_w the molecular weight of water, σ the surface tension of the droplet relative to air (Gibbs free energy per unit area of drop surface), ρ the drop density, R the universal gas constant, T the Kelvin temperature, r the drop radius, n the number of ions formed when the solute is fully dissociated, ϕ the osmotic coefficient (function of chemical species and concentration of solution), and f the molality of the solution. It can be seen that S involves a balance between opposing effects. Lowering the radius while keeping everything else constant increases the saturation (because of the effect of radius of curvature on the free energy). On the other hand, increasing the concentration of ions lowers the equilibrium vapor pressure in accordance with Raoult's Law. The second term on the right side of Eq. (3-1) can often exceed the first, so that droplets of highly concentrated solution can form and be in equilibrium at relative humidities less than 100%. This is the phenomenon known as deliquescence; it accounts for such familiar facts as the stickiness of table salt in muggy weather (the equilibrium relative humidity for a saturated NaCl solution at 25°C is 72%).

The theory for insoluble particles, or mixed particles consisting of soluble and insoluble material is more complex. The case of spherical particles has been treated by Fletcher (1958); he found that the critical saturation ratio was a function of particle radius and contact angle between a water drop and the bulk material. This latter is a quantitative measure of the "wettability" of the substance; a contact angle of zero means the water spreads out on the surface as thinly as possible, while one of 180° means the drop remains spherical and does not wet the surface at all. The equilibrium saturation ratio decreases with increasing particle radius and with decreasing contact angle, but can never be less than unity as is the case for soluble CCN.

On the basis of this brief and incomplete exposition of the theory, it is possible to determine that effective CCN have these characteristics:

(1) Easily wettable (especially if insoluble).
(2) Highly soluble in water.
(3) High degree of dissociation into ions in solution.
(4) Large number of ions per molecule.
(5) Highly hygroscopic (low deliquescence humidity).
(6) Large size.

From the above, it is easy to see that highly polar substances such as acids, bases, and salts of low molecular weight and high solubility are the most effective CCN, although insoluble particles that are highly wettable can be moderately effective.

Examples of good CCN include phosphorus pentoxide, sulfuric acid, nitric acid, aluminum chloride, ammonium nitrate, ammonium sulfate, and alkali chlorides, sulfates and nitrates. Particles with diameters greater than 1 or 2 μm (so-called giant particles) are most effective in generating large cloud droplets. However, the rate of loss of particles to the earth's surface by sedimentation increases with particle diameter, so that the larger particles have a shorter time to act as nuclei.

The criteria for effective IN are less clear-cut. In principle one can apply the general statement of thermodynamic equilibrium, namely that the Gibbs free energy must attain a stationary value. Unfortunately, some important parameters such as the interfacial energy between a crystalline solid and liquid water are hard to determine and are not at all constant over the particle surface. The situation is further complicated by the fact that particles can nucleate ice crystals in three ways, viz.,

(1) Deposition. Water vapor molecules attach themselves to the particle to form a monolayer, after which successive layers build up to form an ice crystal directly from the vapor phase.
(2) Contact freezing. The particle impinges on a supercooled droplet and initiates freezing, either at the point of contact or after entering the droplet.
(3) Condensation-freezing. The particle acts first as a CCN to grow a drop and then as an IN when the temperature is sufficiently low.

The weight of the evidence is that (2) and (3) are the most important mechanisms, but that (1) may contribute significantly at lower temperatures in cloud tops.

It is apparent that the thermodynamic parameters for (1) will differ from those of (2) and (3). They will also be different for crystals of different habits (axis ratios). Some attempts to predict this activation temperature as a function of nucleus properties have been carried out (e.g., Fletcher 1958, 1970). They result in highly complicated formulae that will not be given here. Some qualitative conclusions from the theory are these:

(1) Wettability is a favorable factor for ice nucleation.
(2) Epitaxy (approximately equal spacing of atoms in the crystal lattice of the nucleus and in one plane of the ice crystal) is a favorable factor and is probably essential for deposition nucleation.
(3) Insolubility in water is generally favorable because of the freezing-point lowering effect of solutes. However, soluble substances with large negative heats of solution can chill droplets to the spontaneous freezing temperature.

(4) Except for some biological IN, all effective substances are crystalline solids. Glassy, amorphous substances can be eliminated as possible IN. Some pure substances that are effective ice nuclei are given below.

Inorganics: Silver iodide, lead iodide, cupric sulfide, cupric and cuprous oxides, aluminum oxide.

Organics: Metaldehyde, phloroglucinol, 1-5 dihydroxynaphthalene, copper acetylacetonate. Urea acts as a pseudo-IN by virtue of its high negative heat of solution.

Biological: Some bacteria (Pseudomonas syringae, Erwina herbicola); unidentified constituents of decomposing leaf tissue (Schnell 1976, Schnell and Vali 1976, Vali et al. 1976).

Natural IN consist mainly of crystalline soil minerals of various kinds (e.g., kaolinite). The biological IN mentioned above are the only non-crystalline IN discovered to date. Because the precise nature of the nucleation sites on these biological particles has not yet been determined, the possibility that they too are crystalline remains open.

The apparent common factor for high ice-nucleation efficiency of organic compounds is the presence of one or more polar groups such as -COOH, -CHO, =CO, or -OH in the molecule.

4. BACKGROUND NUCLEUS CONCENTRATIONS: SOME QUANTITATIVE CONSIDERATIONS

The environmental impact of introducing nuclei to the atmosphere, or removing existing nuclei, will obviously depend in some way (not necessarily simple) on the amount of increase or decrease relative to preexisting background levels. This section is devoted to obtaining reasonable estimates of present-day global background concentrations of tropospheric aerosols and nuclei.

Natural atmospheric aerosols arise from several sources: wind-raised soil particles, evaporated sea-spray, volcanoes, forest fires, meteorites, and oxidation of gases such as SO_2 and organic vapors emitted by living and decaying vegetation. All of these sources are subject to considerable variation with time and meteorological conditions. The sink strength also varies with time, location, and altitude. The main mechanism for removal of tropospheric aerosols is precipitation scavenging; the particles may serve as nuclei or may simply be swept out by the falling rain or snow. The mean residence time of a particle is a function of the annual precipitation total; aerosols dispersed in arid climates will persist longer than those in more moist regions.

As of 1971 the global annual direct production of atmospheric aerosol was estimated to be in the range 425 to 1,100 million (M) metric tons (t) per year; the additional source due to gas-to-particle conversion was estimated as 345 to 1,100 Mt/yr. The human contributions were estimated at 10 to 90 Mt/yr for direct generation and at 175 to 325 Mt/yr by gas-to-particle conversions (SMIC 1971, p. 189). The range and mean for the natural sources are 770-2200 and 1485 Mt/yr and those for the anthropogenic are 185-425 and 300 Mt/yr. So as of 1971 the total mean aerosol production was 1785 Mt/yr of which about 20% was anthropogenic.

Estimates of tropospheric residence time have been made by, among others, Weickmann and Pueschel (1973). They arrived at a range of 1 yr to 5.25 h and a mean of about 8.75 days (d). In view of the wide spread of these figures, the round figure of 10 d is assumed in this report.

The theory of first-order processes leads to the simple relation between mean loading Q (Mt), mean (1/e) residence time τ(yr), and source strength S (Mt/yr):

$$Q = \tau S \qquad (4\text{-}1)$$

With τ = 10 d or 0.0274 yr and S = 1,785 Mt/yr one obtains Q = 48.9 Mt as the mean global atmospheric aerosol burden. Some of this is located in the stratosphere where (because precipitation scavenging does not occur) the residence time is several years. Except in years with strong volcanic eruptions, nearly all of the aerosol is in the troposphere. Assuming a mean tropopause height of 13 km and a mean Earth radius of 6,371 km, and noting that the volume of a thin spherical shell of thickness Δr and inner radius r is given by

$$\Delta V = 4\pi r^2 \Delta r \qquad (4\text{-}2)$$

one obtains a tropospheric volume $V = 6.63 \times 10^{18}$ m^3. Dividing this into the burden $Q = 4.89 \times 10^{13}$g or 4.89×10^{19} µg, gives a mean aerosol concentration of 7.4 µg/m^3 as a background level for the troposphere. Most of this is found in the boundary layer (lowest 1 km or so of the troposphere) and over continents, although Saharan and Indian dusts are frequently found throughout the entire depth of the troposphere (Bryson and Wendland 1970, Allee et al. 1976). Generally, the background loading above the boundary layer and over the oceans is of order 0.1 µg/m^3; in urban-industrial areas it is of order 100-300 µg/m^3 and can exceed 1,000 µg/m^3 during some stagnation episodes.

If all of the aerosol particles were active as IN or CCN, there would be no reason for any concern about global impacts of manufactured chemicals or precipitation because the combined releases of all chemicals to the atmosphere would have to be at least of the same order of magnitude as the existing source strength of 1,785 Mt/yr to have any appreciable effect. Measurements show, however, that only a small fraction of the total aerosol population serves as nuclei. Data taken within the boundary layer over the North Atlantic and Mediterranean by Hoppel (1979) show concentrations of CCN active at 0.16% supersaturation in the range 100 to 3,000/cm^3 with a (geometric) mean near 700/cm^3. No IN measurements were made on this cruise. Allee et al. (1976) made CCN and IN measurements aboard aircraft over the North Atlantic above the boundary layer during the BOMEX and GATE field programs and obtained CCN counts (at 1% supersaturation) of 10 to 200/cm^3 with a mean near 100/cm^3. Their IN counts covered the range 1 to $9/\ell$ (1,000 to 9,000/m^3). They also made measurements in the boundary layer at an altitude of 600 m over Florida and found CCN counts in the range 240 to 2,500/cm^3 and IN counts of 10^3 to 10^4/m^3. Recent measurements in Colorado cumuli (Heymsfield et al. 1979) gave low IN counts in the range 50 to 500/m^3.

For CCN, a representative mean concentration of 100/cm^3 appears to be reasonable. If one assumes a characteristic mass of 10^{-15} g (corresponding to a spherical particle of diameter 0.1 μm and bulk density of 2 g/cm^3) one obtains a mean mass loading of 0.1 μg/m^3. Thus apparently only about 1.35% of the tropospheric particles act as CCN below 1% supersaturation. Taking this fraction of the annual aerosol production rate gives 24.2 Mt/yr for the mean rate of generation of CCN; multiplication by the residence time of 10 d (0.0274 yr) yields a mean tropospheric CCN burden of 663 kt (kilotonnes).

It is less easy to arrive at a reliable mean concentration of IN because measurements of IN in air and measurements of ice-crystal concentrations in clouds show wide discrepancies. The IN measurements cited above suggest a mean value of order 5,000/m^3. On the other hand, ice-crystal counts in clouds are frequently higher than this figure. Koenig (1963) reports one case in which the measured number of ice particles with diameters greater than 100 μm was 2 x 10^5/m^3 while at the same time the number of IN active at temperatures warmer than -20°C was only 5,000/m^3; the number of ice particles was 40 times greater than the available nucleus supply. Mossop et al. (1968) measured ice particles in a cloud whose coldest temperature was -4°C and found an approximate mean count during a cloud traverse of 4 x 10^4/m^3 when the cloud reached maturity. IN counts on air samples taken below cloud base showed zero IN active at -4°C, 100/m^3 active at -15°C, and 1,000/m^3 active at -20°C. In an effort to circumvent the problems involved in catching and sizing particles on board an aircraft, Koenig (1968) sampled orographic clouds over the California Coast Range at a fixed mountain-top location and found concentrations of ice crystals in the range 3 x 10^4 to 4 x 10^5/m^3 in clouds with top temperatures around -8°C. On the other hand, the observations of Heymsfield et al. (1979) that were carried out only in the updraft portions of relatively young clouds yielded ice-particle counts of the same order (50 to 500/m^3) as the IN counts. However, the sample is rather small to be statistically significant.

The large discrepancies cited above have been explained by various investigators (Koenig 1963, 1968, Hallett and Mossop 1974, Hobbs 1969, Mossop 1976, Mossop and Hallett 1974, Mossop 1978) as being due to ice-crystal multiplication processes of various kinds. These processes involve the breaking off of ends of crystals or of spicules formed when droplets freeze on contact with other crystals or nuclei; the small fragments then grow into new large crystals. On the other hand, the techniques for in-situ measurements of both IN and ice particles on board aircraft are rather imperfect, so that the data may have substantial errors. It is also possible that ground-based IN counts may not be representative of in-cloud conditions.

Since this whole question will probably not be resolved for some time, a figure of 10^5 IN/m^3 effective at temperatures warmer than -20°C will be assumed as an upper bound to the mean tropospheric IN loading. Assuming again a mean particle mass of 10^{-9} μg, the IN mass loading works out to be 10^{-4} μg/m^3, or (1.35×10^{-4})% of the total particulate loading. This corresponds to an annual IN production rate of 24.1 kt/yr and a mean tropospheric burden of 663 t.

5. SENSITIVITY OF PRECIPITATION TO VARIATION IN NUCLEUS CONCENTRATIONS

The figures arrived at in the previous section can serve as a crude measuring-stick for assessing the impact of adding new nuclei to the atmosphere. If anticipated annual releases of chemicals to the atmosphere are smaller than the present source strength, then there is no need to be concerned about significant modification of global precipitation patterns. On the other hand, if the expected releases are larger than the current source strength, then the possibility of significant weather modification effects must be investigated. The question immediately arises: how great an increase in nucleus concentration is required to produce a significant change in global or regional precipitation? Unfortunately, the existing data are much too sparse to provide a truly definitive answer to this key question. The best that can be done is to make an educated guess based on a limited number of field studies and well-designed intentional weather-modification experiments.

First of all, it must be stated categorically that there is no sound evidence whatever that man's emissions of waste chemical substances to the atmosphere in aerosol form (i.e., the 300 Mt/yr referred to in the previous section) have had any effect on global precipitation totals. If there have been any such effects, they are totally buried in the natural variability of precipitation.

Inasmuch as most of the anthropogenic aerosol is introduced into the atmosphere from the approximately 2.5% of the Earth's surface that is occupied by urban-industrial complexes in the developed countries (Weickmann and Pueschel 1973), one should look first for regional rather than global effects of man-made aerosols on precipitation. Several claims for such effects have been made; there is, however, only one fairly complete field study of a metropolitan area that has been carried out up to this time. This is the METROMEX project, whose objective was to determine as quantitatively as possible the total climatic impact of the St. Louis metropolitan area. Past climatic records within the region and at greater distances were supplemented by ground and airborne measurements of many variables, including IN and Aitken-particle counts. CCN were apparently not measured routinely, but were said to comprise roughly 10% of the total particles measured by the Aitken counters. The Aitken counts in the boundary layer at 600 m AGL upwind of the urban-industrial area averaged around 16,000/cm^3, increasing to about 70,000/cm^3 downwind, a nearly fivefold increase. It may be assumed that the increase in CCN was at least of the same order.

In the case of IN, counts of particles active at -20°C were greater than $10^5/m^3$ in relatively small plumes associated with industrial sources and the downtown area. Upwind background levels were not given in the project report (Ackerman et al. 1978, Part C); one can only assume that they were below $2.5 \times 10^4/m^3$. Thus the plumes contained at least 4 times the background level; the ratio is probably more like 10.

The urban effect on summer rainfall for the years 1972-1975 was studied using data from a dense rain-gauge network. A persistent excess in the northeast and southeast quadrants (downwind in most precipitation situations) relative to the western (upwind) region was noted. Rainfall to the east control area ranged from 90 to 100 cm during June through August; the range in the west was 80 to 90 cm. The urban effect was thus an approximate 10% increase downwind. Studies of the distribution of the increase show that it is quite local; most of it is contained within 40 km of the city center, and the effect is lost in the noise at about 80 km to the east. Much of the downwind excess was found near concentrations of heavy industry; increases of more than 100% above upwind levels were found in small local areas (Changnon et al. 1977, Part B).

This study has shown that a metropolitan area does tend to increase precipitation locally, at least in summer. The increase, however, cannot be tied directly to the downwind increases in nuclei, except to say that in some cases (but not all) the local precipitation maxima lie near the spots with highest Aitken counts. It is likely, however, that the heat and water-vapor outputs from the industrial sources have at least as much to do with the augmented precipitation as do the excess nuclei.

Analysis of radar measurements showed that 45% of these summer cumuliform clouds had first echoes (corresponding to regions of precipitation-size drops) that lay entirely below the 0°C isotherm (Braham and Dungey 1976). This indicates that the coalescence process is active in initiation of precipitation in summer cumuli. One might therefore expect that clouds nucleated by the plumes from industrial sources would be less apt to generate rain by coalescence and that the first echoes would appear at higher elevations. While this tended to be true of organized cloud systems, isolated clouds tended to have lower first echoes when they formed in the pollution plumes. Thus the role of the excess industrial nuclei in augmenting summer rain in the St. Louis area is not at all clear even though an urban-industrial effect on precipitation in a small downwind region is well-established.

Other observations suggest possible effects of steady aerosol emissions on regional precipitation. Parungo et al. (1978) made measurements of the size distributions, morphology, chemical composition, and nucleation activity of aerosols emitted from the stacks of a large copper smelter west of Salt Lake City, Utah. They found that most (∿70%) of the particles in the plume contained sulfur; much of this was in the form of H_2SO_4 haze. The percentage of small sulfate particles tended to increase downwind, indicating that new H_2SO_4 haze droplets were being formed from the SO_2 in the plume. Total Aitken counts (at 200% supersaturation) ranged from $1.66 \times 10^5/cm^3$ at 3.2 km downwind to 1.7×10^4 at 30 km. CCN measurements were not made at the time because of instrument malfunctions, but later laboratory tests on collected aerosol samples indicated that about 50% of the particles were active as CCN. Background (upwind) Aitken counts were of order $300/cm^3$.

This smelter began operations in 1904, but emission inventories of sulfur are available only since 1941. Peak outputs of S were about 1,900 t/d in 1941 and have decreased to about 200 t/d in 1978 as a result of emission-control measures. If one assumes that all of this S is converted to H_2SO_4 and other sulfate salts, and that half of these are active as CCN at less than 1% supersaturation, then the annual source strength for CCN has ranged from 1.06 Mt/yr in 1941 to 0.112 Mt/yr in 1978.

Measurement of IN in the plume showed increases in concentration with distance downwind from the stacks. This is due to poisoning of the IN by adsorbed oxides of sulfur and H_2SO_4. These poisons evaporate as the aerosol ages so that more IN become active as the plume drifts downwind. This was confirmed by exposing samples of the aerosol to vacuum evaporation and to baking at 200°C. The treated samples increased in -20°C nucleating activity by as much as 600% for particles collected near the stack, but treating produced no increase in activity for particles collected 30 km downwind, showing that the poisoning had completely disappeared by then. IN concentrations at 30 km downwind were found to be about 7 x $10^4/m^3$. The ratio of IN to total Aitken particles was approximately 1 particle in 2,100 active at -20°C after aging.

From this data one can estimate the annual production rate of IN. Given the sulfur output and the approximation that this constitutes 70% of the total aerosol by mass, the aproximate IN source strength of this single source has decreased from 471 t/yr in 1941 to 49 t/yr in 1978.

Analysis of precipitation records for Utah show that there was a rather abrupt increase in precipitation in 1904. The mean annual statewide precipitation for the period 1892-1904 was 27.43 ± 3.81 cm. (The spread is one standard deviation each side of the mean.) The corresponding figures for 1905-1946 were 36.0 ± 6.81 cm, an increase of 8.57 cm or 31.24%. After the emissions control program was instituted, the mean for 1945 to 1978 was 28.1 ± 5.1 cm. When only the Colorado river basin region of the state (the area most frequently downwind of the smelter) is considered, the 1892-1904 figures are 19.48 ± 3.78 cm and those for 1905-1949 are 30.51 ± 5.74 cm, an increase of 11 cm or 56%. It thus appears possible that the very high emissions that prevailed during the period 1904-1941 may have brought about a non-trivial (and beneficial) increase in downwind precipitation in this arid region.

A follow-up study (unpublished) suggests that the regional effect may not have been quite so large. When precipitation records for the neighboring state of Idaho were examined, it was found that the mean annual precipitation for the state as a whole for 1892-1904 was 44.5 ± 5.9 cm and that for 1905-1949 was 46.15 ± 6.8 cm, an increase of 1.65 cm or 3.7%. This is not statistically significant. When, however, only the southeastern part of the state, which is climatically similar to the Colorado River Basin of Utah, is considered, the figures for the two periods are 29.7 ± 4.9 cm and 33.2 ± 6.8 cm, an increase of 3.5 cm or 11.8% as an approximation of the "natural" difference of the two periods. Furthermore, the jump in precipitation in 1904 appears to have been a continental or even a global event. So, while it is possible that the smelter effluent may have caused a 45% increase in precipitation during the years 1904-1949, the statistical significance is not sufficiently high to induce much confidence in this conclusion. The drop back to approximately the pre-1904 levels of precipitation after the introduction of emissions control gives a little more support to the possibility of an effect, and also indicates that present levels of emission are not affecting precipitation significantly.

Another source of data relevant to the question of human influences on precipitation can be found in the data from various intentional weather-modification experiments that have been carried out all over the world in the last thirty-odd years. These experiments have involved seeding of clouds with IN or CCN for the purposes of precipitation enhancement or hail reduction. The operational procedures have varied; in some cases individual clouds were seeded internally from aircraft, and in others whole cloud systems were seeded for extended periods from arrays of ground-based IN generators. Silver iodide (AgI) was the most frequently used substance. It has a nucleation threshold of -4°C and, with the usual methods of dispersal, yields about 10^{14} to 10^{15} nucleating particles per gram of AgI, active at -20°C or warmer. For some of the experiments, the amounts of AgI emitted are well-documented.

In one of the longest and best conducted rain-enhancement projects (Gagin and Neumann 1974), winter storm systems in Israel were seeded with AgI. Increases in rainfall of as much as 20.5% in seeded areas relative to control areas were noted. The seeding rate was 800-900 g/h of AgI dispersed along a line by aircraft.

These emissions of nucleating agent were, of course, intermittent; the generators were turned on only when suitable clouds were present. The equivalent steady source strength required to maintain the same concentration of IN at all times would be of order 7.5 t/yr emitted from a line source some 60 km in length.

Studies of drop-size distributions and nucleus concentrations in these Israeli cloud systems showed that these particular clouds are particularly amenable to increasing rain by IN seeding. They have an abundance of small CCN and therefore cannot readily generate rain by the coalescence process. On the other hand, their tops are not usually very cold, so that they are lacking in naturally efficient IN. This is not true of the great majority of precipitation-producing clouds. These facts should be borne in mind when considering the apparent large increase in rainfall in response to a relatively low source strength of IN.

In project "Whitetop", carried out by the University of Chicago in the southern part of Missouri (Braham 1966), seeding rates of the order of 2,700 g/h, or 23.6 t/yr, of AgI were used. In this experiment, precipitation on seeded days was actually less than on unseeded days.

The Florida Area Cumulus Experiment (FACE), conducted by the National Hurricane and Experimental Meteorology Laboratory of the National Oceanic and Atmospheric Administration (NOAA), was also a randomized rain-enhancement project in which groups of developing cumuli were seeded from aircraft (Woodley et al. 1977). Typical seeding ranges were 3,000-4,000 g/d of AgI, for an equivalent annual emission rate of 1.1-1.4 t/yr. However, because the releases were localized inside the clouds, this is equivalent to a far higher diffuse source strength. This is also true for "Whitetop". Precipitation data showed a positive seeding effect of 70%, i.e., seeded days had 70% more precipitation on the average than unseeded days. However, the statistical significance of the increase has been questioned (Nickerson 1979). He showed that natural variability in Florida precipitation could account for the observed seed/no-seed ratios.

- Several experiments on so-called orographic cloud systems (clouds formed in air that is flowing over mountains) have been carried out. The advantage of working with these clouds is that they are always in the same place and that one can sample them with ground-based equipment. A 17-yr program of seeding such clouds over the California Coast Range in the Kings River watershed (Henderson 1968) used 25 AgI smoke generators distributed within a 3,000 km^2 area with outputs of 12 g/h each; the equivalent source strength is 2.6 t/yr. Stream runoff was used as a measure of seeding effect; two neighboring unseeded watersheds were used as controls. A mean annual increase of 6% relative to the controls was reported.

The Climax project (Grant and Mielke 1967) was carried out on clouds that formed over the Continental Divide in Colorado. The seeding was done with six AgI generators positioned on the ground at various distances between 13 and 59 km from the target area; generator output was 20 g/h. The corresponding steady source strength was 1.05 t/yr. Increases of up to 100% in the target area were claimed when the temperature at the 500-mb pressure level ($\sim$5.6 km ASL) was in the range -11° to -20°C.

Winter storm systems over the Lake Almanor drainage area in the northern Sierra Nevada mountains of California were seeded in another experiment (Eberly and Robinson 1967). Six generators with outputs of 2.7 g/h were positioned within the 500 km^2 watershed; the equivalent annual emission rate was 1.4 t/yr. Seeding effects of up to 80% increases were reported for storms with westerly winds; decreases were noted for southerly winds.

In addition to experiments and operational programs for increasing precipitation, there have been several that had as their purpose the reduction in hailfall, or decreasing the size of hailstones. The rationale behind these experiments is that heavy seeding of growing cumulonimbus clouds with IN will result in a larger number of smaller ice particles and also a reduction of available supercooled liquid water so that ice particles cannot grow to large sizes by riming. In these operations, the desired IN concentration is considerably higher than in the case of "rainmaking". In some countries, notably the USSR, the AgI is delivered to the desired part of the cloud by rocket or artillery shell. In other countries where the hazards of falling shrapnel from these carriers is considered too great, the shotgun approach, using large numbers of ground-based AgI aerosol generators, is used. The largest operational program is in France. It has been in operation since 1952, with the object of protecting some crops with high cash value, namely, wine-grapes and tobacco. At present, the seeding network comprises 482 generators distributed over 7×10^4 km^2 in the southwestern and central parts of the country. The emission rate is 13.6 g/h of AgI. If all generators were operating at once, the emission rate would be 6,554 g/h, or 28.7 t/yr. However, the Meteorological Service alerts only the part of the network where the probability of large hail is high, so this figure is not achieved in practice. Fortunately, the project keeps an AgI inventory, so that the actual usage is known for each year. For the last decade, the maximum emission was 4.379 t in 1971; the minimum was 0.736 t in 1974 (Anonymous 1978).

Because the only concern of the organization that conducts the operation is reduction of hail damage to crops, the amount of insurance claims filed is the only statistic used for verification of the program's effectiveness. However, if any major effect on precipitation had occurred, it would have shown up in the Meteorological Service records and would have received comment in the literature. No such comment has been published. Even the effectiveness of the program in reducing hail has been questioned (Boutin 1970) and reaffirmed by the chief scientist of the project (Dessens 1974).

Some attempts have been made in low latitudes to increase precipitation from warm clouds by seeding with large and giant CCN. Common salt (NaCl) ground in a ball mill at high temperature and kept dry until dispersed, was the source of CCN. One such experiment, in the Rio Nazas catchment in Mexico (Fournier d'Albe and Alemán 1976) involved seeding of clouds in a 2×10^4 km^2 region with about 1 t/d of salt for an annual rate of 365 t/yr. The effect on rainfall, a slight decrease on seeded days relative to unseeded days, was statistically insignificant. A similar experiment on summer-monsoon clouds in India (Kapoor et al. 1976) involved salt releases of up to 1,975 kg/d; duration of seeding was up to 3 h 40 min. Assuming that these two maxima occurred together, the seeding rate was 4,694 t/yr. Statistical analysis gave a 16.5% increase relative to one control area in 1974 and 17.3% and 38.6% relative to two controls in 1973, but neither result is statistically significant.

The experiments reported above have shown that concentrated IN sources with strengths of the order of a few tons per year can affect local or regional precipitation totals at barely satisfactory level of statistical significance, under favorable circumstances. On the other hand massive CCN sources do not appear to have any detectable influence on precipitation.

In order to obtain an estimate of nucleus source strengths that would be needed to produce detectable changes in precipitation on a global scale, it is useful to calculate the emissions used in the various cloud-seeding experiments on an areal basis. This has been done by Weickmann (unpublished internal report 1968); the figures are given in Table 1.

Table 1. Source Strengths of AgI Emissions Per Unit Area for Various Cloud Seeding Projects

Project	Source strength ($g/h/km^2$)
Snowy Mountain	0.4
Canadian rain-making	0.5
Whitetop	1.5
Swiss hail suppression	0.07
Bavarian hail suppression	0.25
French hail suppression	0.35
Argentine hail suppression	0.1
Various commercial seeding operations	0.01 to 0.11
Gunn et al.	25
ACN Chicago*	150
Australian rain-making	10
Kraus-Squires cumulus seeding*	300
Florida cumulus (J. Simpson)	800
Australian convective cloud seeding	0.15

*Dry-ice seeding actually used; conversion to AgI is based on laboratory comparisons of number of ice crystals formed by the two techniques.

This table shows that seeding rates, expressed in this way, have been highly variable. In projects where the seeding has been done with ground-based generators distributed over an area, the figures are low, while in projects involving treatment of individual clouds they are higher.

The total global emission that would be required to give the same elevation of IN concentration as was achieved in the various projects is arrived at by multiplying the areal emission rates by the surface area of the earth, 5.1×10^8 km^2. Considering only the projects that used networks of ground generators distributed over an area, one gets total source strengths in the range 5.1×10^7 to 1.78×10^8 g/h, or 0.45 to 1.56 Mt/yr. If it is assumed that releases occur only over land and that all influences on precipitation also occur only over land, then the figures are reduced to about one-third of the above, or 150 to 520 kt/yr. Comparing this with the upper bound of 21.4 kt/yr for current IN production arrived at in Section 5 shows that in order to produce even minimal effects on continental precipitation, the annual IN production rate would have to be increased by at least a factor of from 7 to 24. Furthermore, because 21.4 kt/yr is in fact an upper bound to the current production rate, and because the actual current rate could be as much as two orders of magnitude smaller than that figure, it is very likely that the actual increase in IN source strength required to affect even minimally the world-wide precipitation would be a factor of 1000 or more. Put another way, in order to affect precipitation clouds significantly, the IN concentration must be increased relative to the existing levels by a factor of the order of 1,000.

There is, of course, a great deal of uncertainty in the foregoing analysis. It is unfortunately true that, even after 34 years of cloud-seeding experience, we still have no firm quantitative relationship between IN concentration and precipitation. The figures presented in this report are the best estimates that can be reached on the basis of the very uncertain data base available to us.

An estimate of total continental CCN production can be arrived at on the basis of Braham's (1966) figure of 2 to 4 x 10^1 CCN/cm^2/s for the St. Louis area emission rate. Taking a mean particle mass of 10^{-15} g, multiplying by one-third of the planetary surface area, and converting to an annual basis gives an equivalent source strength of 2,144 Mt/yr. However, as Braham points out, there is a systematic increase in precipitation downwind of the city in spite of the fact that clouds over the city do have narrower drop-size distributions and smaller mean drop sizes than upwind clouds. Clouds 10 to 40 km downwind have already lost those characteristics and contain the usual number of larger drops. Braham suggests that this may be due to a higher percentage of giant CCN in the urban aerosol relative to the upwind aerosol. On the other hand, Ochs and Semonin (1977), using a mathematical model of cloud development containing nucleation microphysics, found that in-cloud processes were insensitive to the presence of giant CCN in concentrations found at St. Louis. It is therefore still uncertain whether or not the CCN concentrations existing at St. Louis are influencing even the local precipitation.

The unsuccessful Rio Nazas experiment had a CCN release rate of 0.02 t/km^2/yr. Multiplying by the approximate planetary land area of 1.7 x 10^8 km^2 gives 3.4 Mt/yr, much less than the St. Louis emission rate. On the other hand, most of these CCN were in the giant size category and should have been more effective in modifying the clouds.

Comparing the St. Louis emission figure with the estimated existing global production rate of 24.2 Mt/yr shows that an increase of CCN production by a factor of 89 above current background is insufficient to produce an unequivocal effect on warm-cloud precipitation. Again, the uncertainty is great, but it appears that CCN emission rates would have to be increased by a factor of >100 to have any significant impact whatever.

Unfortunately, no data exist for assessment of the nucleus-poisoning hazard. Parungo et al. (1978) did observe that the concentration of IN in the plume of the Utah copper smelter increased by a factor of slightly more than two as the aerosol moved from near the stack to 35 km downwind, and that if the aerosol samples collected near the stack were outgassed the IN activity increased sixfold. So for this particular type of poisoning by oxides of sulfur and H_2SO_4, the effect was only temporary, and natural outgassing soon restored the particles to full activity.

Since the only nucleus poisons that are likely to attach themselves to aerosol particles in the atmosphere are gases or condensible vapors, it follows that when the affected particles move to lower concentrations of the gas or vapor the volatility of the absorbed poison will eventually cause it to leave the nuclei. It therefore appears safe to conclude that no global nucleus-poisoning problem will arise, and that local effects will be restricted to the vicinity of concentrated sources of nucleus-poisoning vapors or gases.

6. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn on the basis of the information given in the previous sections.

(1) The potential impact of man-made chemicals on precipitation is by virtue of their droplet or ice nucleating ability or their action as poisons of nuclei.

(2) In order to function as nuclei, chemicals must be dispersed into the atmosphere as aerosols with particle diameters in the range of 0.01 μm to a few μm.

(3) Only substances that are dispersed as gases or condensible vapors are likely to act as nucleus poisons. This is because the probability of liquid droplets or particles colliding and coalescing with nuclei is much lower than the probability of adsorption of gases or vapors on particles.

(4) The chemical and physical properties that characterize effective CCN and IN are different. They have been summarized in Section 3.

(5) Estimates of existing burdens and source strengths of nuclei (Section 4) are these: for CCN, 663 kt and 24.2

Mt/yr; for IN, upper bounds of 663 t and 24.1 kt per year.

(6) Examination of the available data from field studies of inadvertent weather modification and cloud-seeding experiments and operations shows that massive injections of CCN of the order of 100 times the background levels have no statistically significant effects on precipitation. Therefore, unless total releases of chemicals in solid or liquid aerosol form to the atmosphere in amounts greater than 2,400 Mt/yr are expected, there will be no need to screen chemicals for CCN activity.

(7) The data for IN are more uncertain; an increase by a factor of from 7 to 24 over the upper bound to the background quoted in (5) above appears to be necessary to cause detectable increases in precipitation, but the factor is probably much higher if statistically significant increases are to be produced. It is therefore proposed (rather arbitrarily) that a criterion of about 10 times the background production rate, or 250 kt/yr, be established as the limit above which screening for IN activity should be required. This figure might have to be lowered if many different substances active as IN eventually become dispersed at the same time, but it will suffice initially.

In consideration of these points, and the characteristics of effective IN, listed in Section 3, the logic scheme, or flow chart, shown in Figure 1 is recommended for screening chemicals as potential precipitation modifiers. Although most of this diagram is self-explanatory, a few additional comments that are too long to fit in the boxes are appended here.

(1) In the top box, "released to the atmosphere" means under normal conditions of use of the chemical. Accidental releases due to fire, explosion, etc., even if large, are unimportant from the weather-modification point of view because any effects will be transient and will not affect long-term precipitation statistics. The short average residence time of tropospheric aerosols and the absence of any recycling reactions such as those involved in the ozone-Freon problem insure that no long-term effects will ensue from transient emissions of active nuclei.

(2) The side-branch at the second box from the top provides for situations in which the primary substance is a gas or vapor that might undergo gas-to-particle conversion by reaction with atmospheric gases. The query "will it react with atmospheric gases?" should have appended to it the qualification "at a high enough rate so that its mean lifetime as a gas is less than the 10-d residence time of tropospheric aerosols."

Most of the questions are very easy to answer and do not require any special tests. There is, of course, the possibility that solid aerosols might undergo reactions that converted them to active IN. Reactions between dry solids and gases, however, are usually very slow except for such things as alkali metals, etc., which are not likely to be dispersed as aerosols. This category of reactions may therefore be dismissed as an acceptably tiny hazard. It follows that very few substances will be dispersed as fine aerosols in quantities greater than 250 kt/yr. Therefore very few, if any, products would require mandatory testing for IN activity.

An obvious exception to the last statement is, of course, stack emissions from chemical factories or processing plants. As has been shown in Section 5, local or regional effects can be (and are) produced by IN emitted as by-products of plants such as ore smelters and steel mills. It is not clear to the panel members whether control of stack emissions is within the scope of the Toxic Substances Control Act. If it is, and if local and regional weather modification is a matter of concern, then airborne in-situ measurements of IN in stack plumes, such as those done by Parungo et al. (1978) in Utah, would be needed.

The problem of nucleus poisoning does not appear to be a serious one. The gaseous poisons such as SO_2 will evaporate off the nuclei once the ambient partial pressure of the poison becomes low. The only persistent poisons would be hazes or mists of nonvolatile, oily, hydrophobic liquids that might collide with and coat IN or CCN. It is hard to conceive of any circumstance in which such substances would be deliberately released to the atmosphere, except possibly as stack effluents. In the latter case, the adverse effects on health and other nuisance effects would demand prompt abatement measures. Therefore the box labeled "Test for nucleus poisoning" in Figure 1 should have appended to it "if releases to the atmosphere will exceed the 250 kt/yr figure proposed as a criterion for solids."

7. TECHNIQUES FOR TESTING NUCLEATION EFFICIENCY

As explained in Section 3, ice nuclei in the air may nucleate ice in clouds by acting as deposition, freezing, or contact nuclei. A deposition nucleus is one on which ice is deposited directly from the vapor phase; a freezing nucleus acts by nucleating a supercooled droplet in which it is embedded; and a contact nucleus initiates the freezing of a supercooled droplet with which it collides. The threshold temperature of an ice nucleus depends on the mechanism by which it nucleates ice as well as its previous history. Consequently, the concentration of ice nuclei in the air that will be active in forming ice in a cloud is an extremely difficult quantity to measure. All the many techniques developed to measure concentrations of ice nuclei active at a

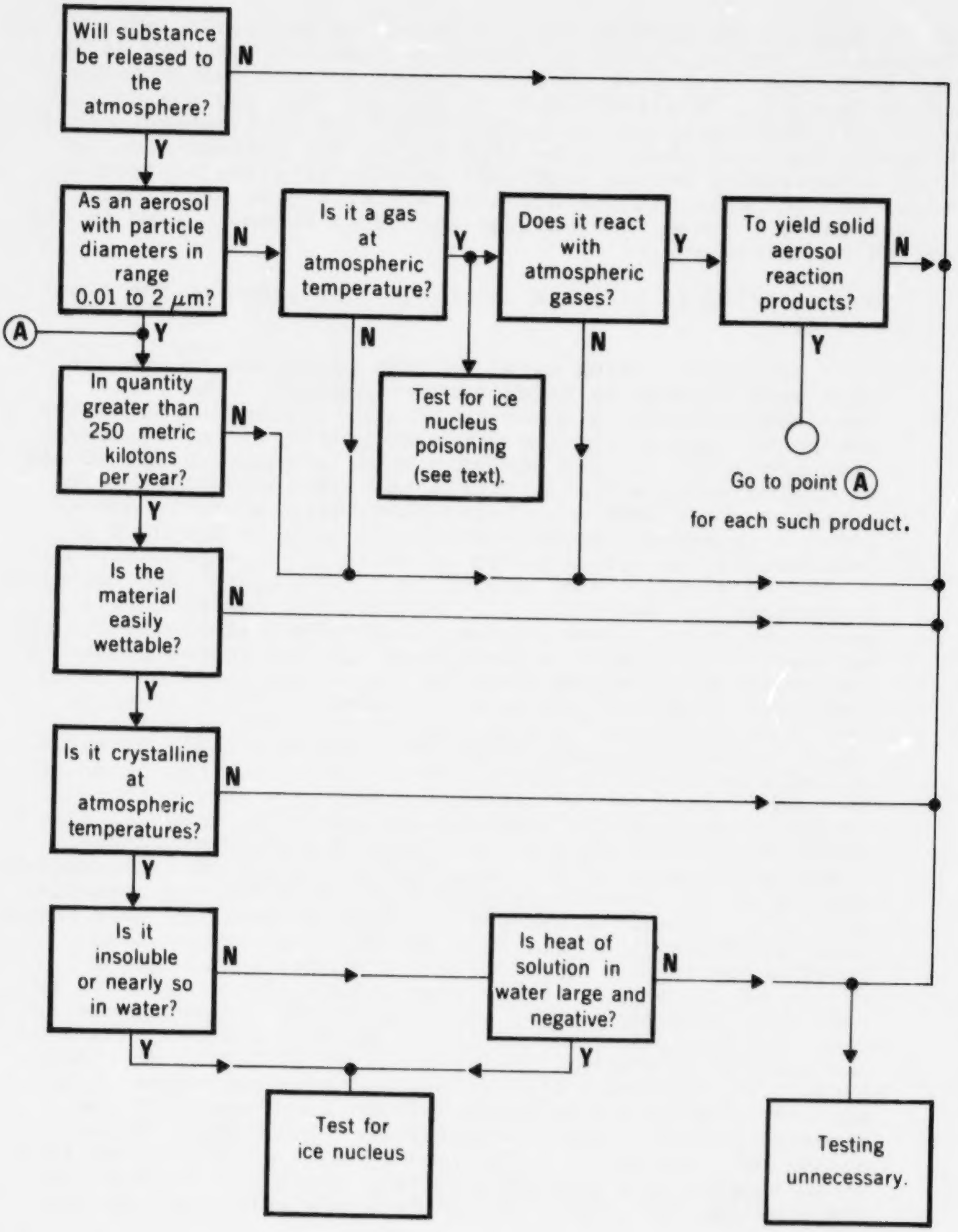

Will substance be released to the atmosphere?
N
Y
As an aerosol with particle diameters in range 0.01 to 2 μm?
N
Is it a gas at atmospheric temperature?
Y
Does it react with atmospheric gases?
Y
To yield solid aerosol reaction products?
N
A
Y
N
Test for ice nucleus poisoning (see text).
N
Y
Go to point A for each such product.
In quantity greater than 250 metric kilotons per year?
N
Y
Is the material easily wettable?
N
Y
Is it crystalline at atmospheric temperatures?
N
Y
Is it insoluble or nearly so in water?
N
Is heat of solution in water large and negative?
N
Y
Y
Test for ice nucleus
Testing unnecessary.

Figure 1. Ice nucleus screening flow chart.

given temperature process the ice nuclei in particular manners. In general, therefore, it is not to be expected that the different techniques will give the same number for the concentrations of ice nuclei in a given sample of air, or that any one of them will give the number of ice nuclei effective in a natural cloud. Probably the best that can be expected at the present time is that a particular device might measure the relative concentrations of ice nuclei in the air that are effective at different temperatures. These reservations should be borne in mind in the following discussion.

Hobbs (1974, p. 631) has described approaches to the study of ice nuclei:

> Ice nuclei which exist as free particles in the air have been studied by three general methods. The first involves isolating a quantity of air, cooling it below the dew-point, and noting the freezing points of the condensation products. In the second method, a known volume of air is cooled until a cloud is produced and the number of ice crystals which form at a particular temperature is determined. In expansion chambers the cooling is produced by compressing the air and then allowing it to expand rapidly. In mixing chambers the cooling is by refrigeration. Several techniques are available for counting the number of ice particles which appear in the cloud. For example, the cloud may be illuminated by a light beam and the concentration of ice crystals estimated visually. Alternatively, the small ice crystals which form in the chamber may be allowed to fall into a dish or film of supercooled water (Cwilong 1947), supercooled soap solution (Schaefer 1948), or supercooled sugar solution (Bigg 1957), where they can be detected and counted by the larger ice crystals they produce. Another technique for counting ice crystals, known as the acoustic particle counter, has been described by Langer (1965) and has been used in an automatic ice nucleus counter (Langer et al. 1967). In this instrument the ice particles which form in a cold box pass through a capillary tube where they produce audible clicks. These clicks are counted electronically and the number of ice nuclei in a given volume of air active at the temperature of the cold box is recorded. The third type of method which has been used for counting ice nuclei in the air is to draw a known volume of air through a membrane filter (Bigg et al. 1963; Stevenson 1968). The membrane filter retains those particles in the air with dimensions in excess of about one-tenth of the diameter of the pores of the filter. The number of ice nuclei on a filter is determined by holding the filter at a known temperature, exposing it to a given supersaturation, and counting the number of ice crystals which grow on it.

A more recent technique for measuring ice nuclei has been developed by Schnell (1979). Aerosols are captured on hydrophobic membrane filters, and the ice nuclei in/on the filter are detected by setting an array of nucleant-deficient water drops on the filter and then cooling the filter. The presence of nuclei on the filters is detected by the freezing of the drops.

Today there are probably 75 unique instruments available for measuring ice nuclei, each with their proponents and detractors. No instrument measures all types of ice nucleation, nor do any of them measure in all of the three general methods. Only the Mee ice nucleus counter is sold commercially, and in 10 years of sales, only 10 have been purchased. The rest of the ice nucleus counters are in experimental laboratories or are used in some field programs to monitor relative changes in ice nucleus concentration. In the latter case, cloud chambers of the NCAR/E. Bollay type are used most frequently (Langer 1965). These counters are no longer being manufactured.

Several international workshops have been held with the express purpose of comparing ice nucleation measurement methods and to find a common ground for measuring ice nucleation modes. These goals have not as yet been attained (Grant 1971, Vali 1976).

The following list presents some key information on sources of ice nucleation measurement techniques and results, as well as comparisons between instruments and techniques that are not listed, discussed, or compared in the two volumes from the International Workshops (Grant 1971, Vali 1976) or are not referenced above.

Cloud chamber comparisons

Isothermal Cloud Chamber Dynamic Cloud Chamber	(Garvey et al. 1976)
Diffusion Chamber	(Schaller and Fukuta 1979)
Diffusion Chamber	(Langer and Rodgers 1975)
Diffusion Chamber	(Jiusto et al. 1976)

Expansion chamber comparisons

Mee Counter CSU Isothermal NCAR Counter	(Langer and Garvey 1980)
Mee Counter	(Hindman et al. 1980)

Drop freezing techniques

Chemical effects on ice nuclei	(Reischel 1973)
Chemical effects on ice nuclei	(Schnell and Vali 1974)

In view of the rather chaotic state of the art, it is not possible to establish a "standard" instrument or procedure for nucleation measurement at the present time; the recommendations that follow are tentative.

The least expensive and easiest-to-implement procedure for IN testing is the method of Schnell (1979). The aerosol to be tested is collected on a membrane filter treated with a hydrophobic coating. The filter is then partially covered with small (millimeter-sized) distilled and deionized water drops and chilled slowly by a thermoelectric cooler equipped with a thermistor or thermojunction for monitoring the filter temperature. The number of drops that freeze in a given temperature interval is recorded by hand. A filter that has not been exposed to the aerosol is processed in the same way to serve as a blank and thus eliminate the effect of the substrate and any impurities in the water.

The cloud-chamber techniques eliminate any possible substrate effect and create a closer approximation to a real cloud environment, but are more expensive and require trained operators. One instrument of this type is available commercially from Mee Industries, Inc., 1629 S. Del Mar Ave, San Gabriel, CA 91776. It is similar to the NCAR/Langer chamber, but differs from it in the technique used to count the ice crystals automatically. The crystals fall between two crossed polarizing filters that are placed between a light source and a photodetector and produce light pulses by virtue of the depolarization associated with crystals.

A very recent design of thermal-diffusion cloud chamber is the "wedge" chamber of Schaller and Fukuta (1979). It has the advantages of being relatively easy to build and being able to detect the mode of nucleation (deposition, condensation-freezing, or contact), as well as the temperature of activation. It is the instrument recommended at present for exhaustive testing for ice-nucleating potential. Unfortunately, it is not in commercial production and the information given in the referenced paper is not complete and detailed enough to serve as a construction manual. Further information about this device may be obtained from Professor Norihiko Fukuta, Department of Meteorology, University of Utah, Salt Lake City, Utah 84108.

For CCN measurement, the thermal-diffusion cloud chamber is the only practical technique at present. Many varieties exist and are described in the two workshop reports (Grant 1971, Vali 1976). They differ in dimensions, methods of achieving thermal and vapor stratification, and in the methods for counting the droplets. Mee Industries produces one such instrument (Model 140) with optical drop counting, continuous analog voltage output, and continuous sample flow. Another commercial version of a chamber originally designed by Radke (Grant 1971, pp. 41-42) is manufactured by Meteorology Research, Inc., Box 637, 464 W. Woodbury Road, Altadena, CA 91001.

In order to reproduce conditions in natural clouds, the supersaturation with respect to water must be low, less than 0.25% or so. Many cloud chambers do not meet this requirement; they operate at around 1%. Fukuta and Saxena (1979) have designed a chamber for CCN counting in which a well-defined spatial distribution of supersaturation is maintained while sample air flows continuously through the system. An optical scanner sequentially examines regions of different supersaturation to give a spectrum of the number of nuclei as a function of supersaturation. Again, this is the preferred instrument for comprehensive testing, but it is not commercially available; inquiries should be directed to Prof. Fukuta.

Techniques for generating test aerosols are described in the nucleation workshop reports (Grant 1971, Vali 1976). Except for materials that decompose irreversibly below their boiling or sublimation temperatures, thermal evaporation is the preferred method. A measured amount of bulk material is made into a paste with pure water and coated on a platinum or Nichrome wire in a clean glass vessel. A clean, dry carrier gas is passed through the vessel. The wire is quickly heated electrically above the vaporization point of the substance under test. The material condenses to a smoke that is transported by the carrier gas into a storage volume, e.g., a Mylar bag contained within a rigid vessel. The aerosol may be allowed to age in the bag so as to coagulate the aerosol into larger particles if desired.

When a test is run, the Mylar bag is squeezed by pressurizing the outer vessel to transfer the aerosol to the cloud chamber or filter. The carrier gas may be air or nitrogen; it must be rendered oil- and water-free by passage through silica gel and then cleaned of all particles by passage through an absolute filter. Provision for monitoring particle size of the generated aerosol is highly desirable when thermal-diffusion cloud chambers are used. This is because particles that act as contact IN must exist in the smaller size range (diameters from about 0.01 μm to 0.1 μm) so that Brownian motion can be effective in bringing them into contact with supercooled droplets in a reasonably short time. On the other hand, CCN are more effective when they are larger than 0.1 μm because no collision process is involved in drop nucleation from the vapor.

For IN, the desired information is the number of nuclei per gram of substance effective in forming ice crystals in various class intervals of temperature from 0°C to -25°C. It would also be desirable to establish the relative effectiveness in each of the nucleation modes, but this is not essential in routine testing. For CCN, the desired data are the numbers of droplets produced per gram of substance at water supersaturations between 0.1% and 1%.

To test for IN poisoning, a sample of a known good IN such as AgI is processed first and the number-vs.-temperature curve recorded. Then another sample is run with the same aerosol mixed with the vapor of the suspected poison, and the decrease, if any, in the numbers of ice crystals formed at the various temperatures is noted.

8. ACKNOWLEDGMENTS

The panel chairman thanks Drs. Helmut K. Weickmann and Russell C. Schnell for assistance in collecting information on emission rates in weather-modification experiments and on the techniques for nucleus measurement.

9. REFERENCES

Ackerman B, Changnon SA, Jr., Dzurisin G. et al. 1978. Summary of METROMEX, Volume 2: Causes of Precipitation Anomalies. Illinois State Water Survey, Urbana, IL.

Allee PA, Sax RI, Delgado E. 1976. Concentrations of Aitken, cloud droplet condensation, and ice nuclei over selected oceanic and continental sites. In: Preprints, International Conference on Cloud Physics, July 26-30, 1976, Boulder, Colorado. American Meteorological Society, Boston, MA, pp. 1-8.

Anonymous. 1978. Programme de prévention contre la grêle. Association Nationale d'Etude et de Lutte Contre les Fléaux Atmospheriques 27:2-20.

Auer AH, Jr. 1975. The production of cloud and Aitken nuclei by the St. Louis metropolitan area (Project METROMEX). J. Rech. Atmos. 9:11-22.

Barrett EW, Parungo FP, Pueschel RF. 1979. Cloud modification by urban pollution: a physical demonstration. Meteorol. Rundsch. 32:136-149.

Battan LJ. 1953. Observations on the formation and spread of precipitation in convective clouds. J. Meteorol. 10:311-324.

Bigg EK. 1957. A new technique for counting ice-forming nuclei in aerosols. Tellus 9:394-400.

Bigg EK, Mossop SC, Meade RT, Thorndyke NSC. 1963. The measurement of ice nuclei concentration by means of millipore filters. J. Appl. Meteorol. 2:266-269.

Boutin C. 1970. Contrôle statistique et contrôle physique des opérations de prévention de la grêle. Thèse 3^{e} Cycle, Faculté des Sciences de Paris.

Braham RR, Jr. 1957. In: Cloud and Weather Modification: A Group of Field Experiments. Meteorol. Monogr. 2(11):67.

_____. 1966. Project Whitetop - A Convective Cloud Randomized Seeding Project. Part I - Design of the Experiment. Part II - Summary of Operations. University of Illinois, Urbana, IL.

Braham RR, Jr., Dungey M. 1976. Effects of a large city upon convective clouds and coalescence rain. In: Preprints, Int. Conf. on Cloud Physics, July 26-30, 1976, Boulder, CO. American Meteorological Society, Boston, MA, pp. 275-278.

Bryson RA, Wendland WM. 1970. Climatic effects of atmospheric pollution. In: Global Effects of Environmental Pollution. Singer SF, ed. Springer-Verlag, New York, NY, p. 130.

Byers HR. 1965. Elements of Cloud Physics. University of Chicago Press, Chicago, IL.

Changnon SA, Jr., Huff FA, Schickedanz PT, Vogel JL. 1977. Summary of METROMEX, Volume 1: Weather Anomalies and Impacts. Illinois State Water Survey, Urbana, IL.

Cwilong BM. 1947. Sublimation in a Wilson chamber. Proc. R. Soc. London, Ser. A 190:137-143.

Dessens J. 1974. La lutte contre la grêle. Commentaires sur une phrase: "Rien ne permet d'affirmer que les interventions aient eu un effet. . . ." Association Nationale de Lutte Contre les Fléaux Atmosphériques 22:43-44.

Eberly DZ, Robinson LH. 1967. Design and evaluation of randomized winter time cloud seeding at high evaluation. Proc. Fifth Berkeley Symp. on Mathematical Statistics and Probability, Vol. V, Weather Modification Experiments. University of California, Berkeley, CA, pp. 65-90.

Fitzgerald JW, Spyers-Duran PA. 1973. Changes in cloud nucleus concentration and cloud droplet size distribution associated with pollution from St. Louis. J. Appl. Meteorol. 12:511-516.

Fletcher NH. 1958. Size effect in heterogeneous nucleation. J. Chem. Phys. 29:572; 1959. Erratum. 31:1136.

_____. 1962. The Physics of Rainclouds. Cambridge University Press, Cambridge, England.

Fletcher, NH. 1970. The Chemical Physics of Ice. Cambridge University Press, Cambridge, England.

Fournier d'Albe EM, Mosiño Alemán P. 1976. A large-scale cloud seeding experiment in the Rio Nazas catchment area, Mexico. In: Papers Presented at the Second WMO Scientific Conference on Weather Modification. (WMO Publication No. 443). Secretariat of the World Meteorological Organization, Geneva, Switzerland, pp. 143-150.

Fukuta N, Saxena VK. 1979. A horizontal thermal gradient cloud condensation nucleus spectrometer. J. Appl. Meteorol. 18(10): 1352-1362.

Gagin A, Neumann J. 1974. Rain stimulation and cloud physics in Israel. In: Weather and Climate Modification. Hess WN, ed., Wiley, New York, NY, pp. 454-494.

Garvey DM, Lilie LE, Grove TC, Grant LO. 1976. Determination of the rates of ice crystal formation in two large cloud chambers. Preprints, Int. Conf. on Cloud Physics, Boulder, Colorado, July 26-30, 1976. American Meteorological Society, Boston MA, pp. 121-125.

Grant LO, ed. 1971. The Second International Workshop on Condensation and Ice Nuclei. Colorado State University, Department of Atmospheric Science, Fort Collins, CO.

Grant LO, Mielke PW, Jr. 1967. A randomized cloud seeding experiment at Climax, Colorado 1960-1965. Proc. Fifth Berkeley Symp. on Mathematical Statistics and Probability, Vol. V, Weather Modification Experiments. University of California, Berkeley, CA, pp. 115-131.

Hall F. 1957. In: Cloud and Weather Modification: A Group of Field Experiments. Meteorol. Monogr. 2(11):33.

Hallet J, Mossop SC. 1974. Production of secondary ice crystals during the riming process. Nature 249:26-28.

Henderson TJ. 1968. Cloud seeding on the Kings River watershed, final report on the 1966-1967 operations with review of results for water years 1955-1967. Report submitted to Kings River Conservation District, Fresno, CA, by Atmospherics, Inc.

Heymsfield AJ, Knight CA, Dye JE. 1979. Ice initiation in unmixed updraft cores in northeast Colorado cumulus congestus clouds. J. Atmos. Sci. 36:2216-2229.

Hindman EE, II, Tag PM, Silverman BA, Hobbs PV. 1976. Calculations of the effects on rainfall caused by cloud condensation nuclei from a paper mill. In: Papers Presented at the Second WMO Scientific Conference on Weather Modification (WMO Publication No. 443). Secretariat of the World Meteorological Organization, Geneva, Switzerland, pp. 21-24.

Hindman EH, Odenkrantz FK, Finnegan WG. 1980. Cloud nuclei from launches of solid rocket boosters. J. Weather Modif. 12 (in press).

Hobbs PV. 1969. Ice multiplication in clouds. J. Atmos. Sci. 26:315-318.

Hobbs PV. 1974. Ice Physics. Clarendon Press, Oxford.

Hoppel WA. 1979. Measurement of the size distribution and CCN supersaturation spectrum of submicron aerosols over the ocean. J. Atmos. Sci. 36:2006-2015.

Jiusto JE, Lala GG, Zamurs J. 1976. Filter measurement of ice nuclei concentrations and selected comparisons. Preprints, Int. Conf. On Cloud Physics, Boulder, Colorado, July 26-30, 1976. American Meteorological Society, Boston, MA, pp. 53-56.

Kapoor RK, Krishna K, Chatterjee RN, Ramana Murty AS, Sharma SK, Ramana Murty BV. 1976. An operational rain stimulation experiment using warm technique over Rihand catchment in northeast India during summer monsoons of 1973 and 1974. In: Papers presented at the Second WMO Scientific Conference of Weather Modification, (WMO Publication No. 443). Secretariat of the World Meteorological Organization, Geneva, Switzerland, pp. 15-20.

Koenig, LR. 1963. The glaciating behavior of small cumulonimbus clouds. J. Atmos. Sci. 20:29-47.

_____. 1968. Some observations suggesting ice multiplication in the atmosphere. J. Atmos. Sci. 25:460-463.

Langer G. 1965. An acoustic particle counter; preliminary results. J. Colloid Sci. 20:602-609.

Langer G, Garvey DM. 1980. Intercomparison of Mee and NCAR ice nucleus counters and the Colorado State University Isothermal Chamber. J. Weather Modif. 12 (in press).

Langer G, Rodgers J. 1975. An experimental study of the detection of ice nuclei on membrane filters and other substrata. J. Appl. Meteorol. 14:560-570.

Langer G, Rosinski J, Edwards CP. 1967. A continuous ice nucleus counter and its application to tracking in the atmosphere. J. Appl. Meteorol. 6:114-125.

Mason BJ. 1971. The Physics of Clouds. Clarendon Press, Oxford.

Mossop SC. 1976. Production of secondary ice particles during the growth of graupel by riming. Q. J. R. Meteorol. Soc. 102:45-47.

_____. 1978. The influence of drop size distribution on the production of secondary ice particles during the growth of graupel by riming. Q. J. R. Meteorol. Soc. 104:323-330.

Mossop SC., Ruskin RE, Heffernan KJ. 1968. Glaciation of a cumulus at approximately -4C. J. Atmos. Sci. 25:889-899.

Mossop SC, Hallet J. 1974. Ice crystal concentration in cumulus clouds: influence of the drop spectrum. Science 186:632-634.

Nickerson EC. 1979. FACE rainfall results: seeding effect or natural variability? J. Appl. Meteorol. 18:1097-1105.

Ochs HT, III, Semonin RG. 1977. The sensitivity of cloud microphysics to an urban environment. Preprints, 6th Conf. on Inadvertent and Planned Weather Modification. American Meteorological Society, Boston, MA, pp. 41-44.

Parungo FP, Pueschel RF, Ackerman E, Proulx H, Wellman D. 1978. Characteristics and meteorological impacts of pollutants from the Kennecott Copper Smelter. NOAA Tech Rept. ERL 395-APCL 42.

Ramana Rao T, Ramana Murty BV. 1973. Effect of steel mills on rainfall at distantly located stations. Indian J. Meteorol. Geophys. 24:15-26.

Reischel MT. 1973. Influences of dissolved salts on the effectiveness of freezing nuclei. Report AR 105, Dept. of Atmos. Sci., University of Wyoming, Laramie, WY.

Schaefer VJ. 1948. The detection of ice crystals in the free atmosphere. Proj. Cirrus Occasional Report No. 9, General Electric Company, Schenectady, NY.

Schaller RC, Fukuta N. 1979. Ice nucleation by aerosol particles: experimental studies using a wedge-shaped ice thermal diffusion chamber. J. Atmos. Sci. 36:1788-1802.

Schnell RC. 1976. Naturally occurring biological ice nucleants: a review. In: Preprints, Int. Conf. on Cloud Physics, July 26-30, 1976, Boulder CO. American Meteorological Society, Boston, MA, pp. 57-60.

_____. 1979. A new technique for measuring atmospheric ice nuclei active at temperatures from -20°C to approaching 0°C, with results. Proc. Seventh Conf. on Inadvertent Weather Modification, Banff, Alberta, Oct. 8-12. American Meteorological Society, Boston, MA, pp. 110-111.

Schnell RC, Vali G. 1974. Heterogeneous ice nucleation in the presence of aliphatic amines and ammonia. Report AR 113, Dept. of Atmos. Sci., Univ. of Wyoming, Laramie, WY.

_____. 1976. Biogenic ice nuclei. Part I: terrestrial and marine sources. J. Atmos. Sci. 33:1554-1564.

SMIC 1971. Study of Man's Impact on Climate. Wilson CL, ed., MIT Press, Cambridge, MA.

Stevenson, CM. 1968. An improve millipore filter technique for measuring the concentrations of freezing nuclei in the atmosphere. Q. J. R. Meteorol. Soc. 94:35-43.

Vali G, ed. 1976. The Third Int. Workshop on Ice Nucleus Measurements. Univ. of Wyoming, Laramie, WY.

Vali G, Christensen M, Fresh RW, Galyan EL, Maki LR, Schnell RC. 1976. Biogenic ice nuclei. Part II: bacterial sources. J. Atmos. Sci. 33:1565-1570.

Warner J. 1968. Reduction in rainfall associated with smoke from sugar-cane fires. J. Appl. Meteorol. 7:247-251.

Weickman HK. 1974. The mitigation of Great Lakes storms. In: Weather and Climate Modification, Hess WN, ed. Wiley, New York, NY, pp. 318-354.

Weickman HK, Pueschel RF. 1973. Atmospheric aerosols: residence time, retainment factor, and climatic effects. Contrib. Atmos. Phys. 46:112.

Woodley WL, Simpson J, Biondini R, Berkeley J. 1977. Rainfall results, 1970-1975: Florida Area Cumulus Experiment. Science 195:735-742.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1981—778-709/228 Region No. 8